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Vol. 29. No. 239. November 1943.

A STUDY OF OIL OXIDATION AS RELATED TO LUBRICATION.* PART I.—APPARATUS, TECHNIQUE, AND PRELIMINARY RESULTS.

By Paul G. Exline, M.S.,† W. E. Kramer, B.S.,† and John R. Bowman, Ph.D.†

The possibility that the surrounding atmosphere may influence lubrication was suggested by the explorations of Gilson,[1, 2] but the rôle of oxidation in lowering friction was first pointed out by King.[3]

It was he who showed that oxidation of a lubricating oil can alter its behaviour in a journal bearing to extend the range of operation beyond that normally secured from the same oil before oxidation. More recently Jakeman and Fogg[4] investigated this effect, using the same machine and following the same procedure, but concluded that "the increase in seizing temperatures and decrease in minimum friction produced by running a bearing periodically up to seizing temperature in oxidizing conditions, are not due to any great extent to a change in the oil, being almost entirely accounted for by changes in the form and surface finish of the bush bearing." In view of the known influence of the higher fatty acids in reducing friction, and of the further known tendency of petroleum lubricating oils to form high-molecular-weight acids on mild oxidation, it appeared that a positive effect of oxidation was to be anticipated. It was believed also that the mechanical variables mentioned by Jakeman and Fogg could be controlled if a sufficiently refined test method could be devised.‡

Several changes were felt necessary in the procedure in order to facilitate rigid control of all conditions.

1. In order to avoid distortion in the bearing and its associated parts due to temperature changes, all such parts should be maintained at a constant temperature.
2. Means should be available for controlling the rate of oxidation of the oil.
3. Under constant-temperature operation of the bearing, the periodic approach to incipient seizure must necessarily be through a steady increase of load or decrease of journal speed. The increasing load method was chosen for reasons of convenience.
4. The point of incipient seizure should have a definite reproducibility and should occur under conditions which would least affect the bearing surface and shape.

* Received March 1942. Presented before The Division of Petroleum Chemistry, American Chemical Society.

† Gulf Research and Development Company and Mellon Institute of Industrial Research.

‡ The experiments described in this paper were carried out following the suggestion of Dr. W. A. Gruse that duplication of this work under carefully controlled conditions might give additional information on a question of major industrial importance, as well as throw some light on the mechanism of oxidation of a lubricating oil.

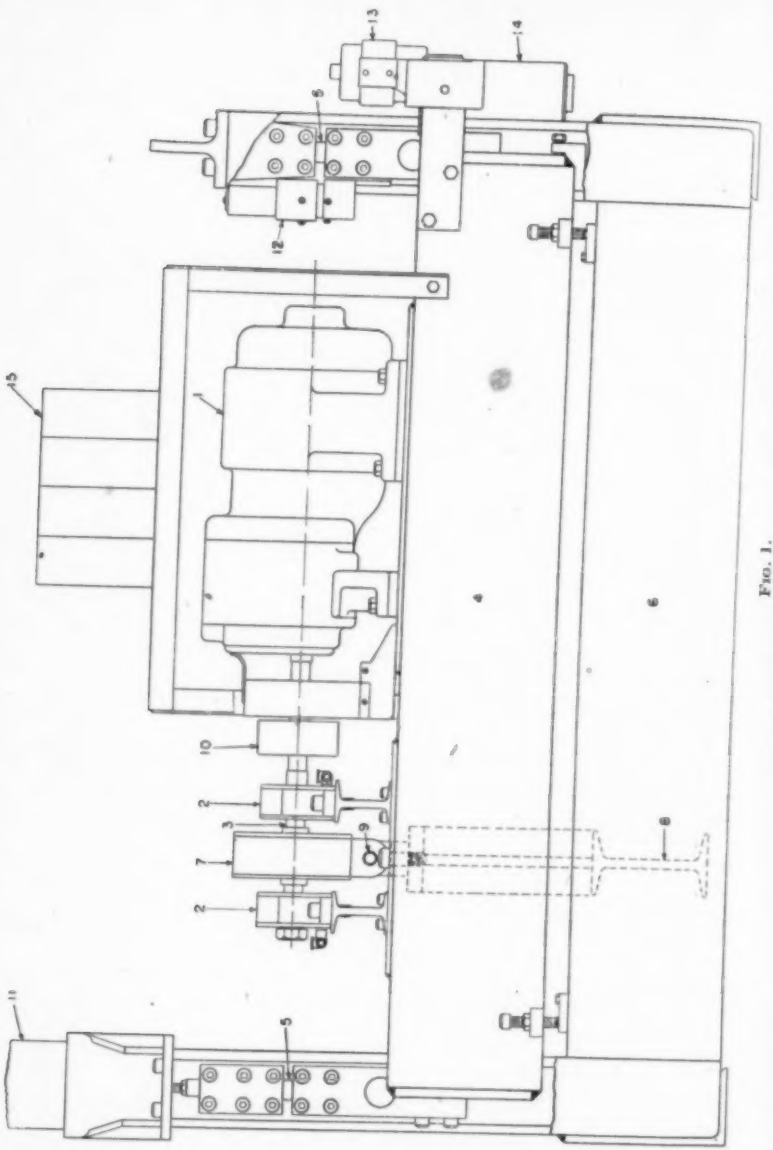

FIG. 1.
SIDE ELEVATION OF BEARING TEST MACHINE.

Description of Apparatus.*

The machine constructed for this purpose applied a load to a bushing in which a journal was driven at constant speed. This load is periodically increased from zero to incipient seizure, while it and the torque are recorded continuously. The atmosphere and temperature of the oil system were under control at all times, and the operation of the machine was entirely automatic.

The instrument, shown in Fig. 1, consists of two parts: the frame and the moving system. The moving system comprises a rigid box-section beam or cradle (4), which is suspended at each end by thin steel tapes (5), and which carries the constant-speed driving motor (1) with an output speed of 107 r.p.m. obtained by gearing, two self-aligning ball bearings (2), the test journal (3), a magnetic clutch (10), and counter-balancing weights (15). The supporting tapes are accurately aligned with the axis of the journal, so that the entire moving system is free to rotate about this axis with a small amplitude.

All electrical connections to the cradle are made through a group of steel pins attached to the frame at (12) which dip into a corresponding group of mercury cups which form part of the moving system.

FIG. 1.
SIDE ELEVATION OF BEARING TEST MACHINE.

Balancing and Torque Recording System.

The frictional torque on the journal is measured by determining the restoring torque applied to the cradle to hold it in a horizontal position. The balancing system is mounted on the rear of the cradle, and consists essentially of a balancing weight (14) on a horizontal screw at right angles to the axis of the cradle and driven by a reversible motor (13). The motor is controlled through a suitable electrical circuit by spring contacts which are closed when rotation of the cradle approaches an angle of 15 seconds. In this manner, torques applied to the journal can be balanced to an accuracy of 0·02 in./lb.

Uninterrupted motion of the balancing weight in one direction for one second of time causes a resistance in series with the motor to be shunted out; this more than doubles its speed. This prevents "hunting" oscillations when the torque is changing slowly, and permits the weight to follow the more rapid change near the end of each cycle.

A continuous record of the torque is obtained on a 10-inch-wide strip chart driven at the rate of 2 in. per hour by a small synchronous motor. Arms projecting from the cradle support the chart drive carriage, which is directly behind the balancing weight, to which is attached the recording pen arm.

At incipient seizure the torque is increasing so rapidly that the balancing weight is unable to maintain the cradle in its zero position. Flexure of the spring contact takes place, and a third or "breakdown" contact is closed when the torque applied to the journal reaches a definite value greater than that of the restoring torque applied by the weight. This contact then acts to stop the journal almost instantaneously by de-energizing the magnetic clutch and reducing the bearing load to zero by the method to be described

* The test equipment was designed following suggestions by Mr. R. J. S. Pigott, Chief Engineer, Gulf Research and Development Company.

later. It has been observed that at incipient seizure the rate of increase of torque is so rapid that the absolute value of the seizing load is little influenced by the speed of travel of the balancing weight.

Loading System.

A rear cross member on the frame carries the upper or fixed portion of the rear tape suspension. A front cross member supports a frictionless hydraulic loading device (11) which carries the upper half of the front tape suspension. Oil pumped into this loading cylinder applies a vertical force to the front tape, about 40 p.s.i. being required to hold the cradle in a horizontal position. An auxiliary device is used for introducing oil into the cylinder at a constant rate. Oil is exhausted from the cylinder through a solenoid valve, which is opened when the breakdown contact is closed and which is closed again by a pressure-operated switch when the cylinder pressure is reduced to 40 p.s.i. This pressure switch also energizes the magnetic clutch, thus starting a new cycle.

The test-bearing housing (7) is supported from the cross member (8) which is attached to the side channels (6) of the main frame. A pin (9) assists in maintaining accurate alignment of the bearing with the journal. The upward pull of the loading device forces the journal against the top of the bearing. This force is zero for a pressure of 40 p.s.i. in the loading cylinder, while the maximum capacity of the machine, 4000 lb., is obtained with 690 p.s.i. in the cylinder. Fig. 2 shows a record of the pressure in the loading cylinder during 37 cycles of a typical run.

Test Bearing.

The test bearing (3) shown in longitudinal section in Fig. 3 is a bronze sleeve 1 inch inside diameter and 2 inches outside diameter pressed into the steel housing (4). The sleeve is $1\frac{1}{2}$ inches long, but is counter-bored to a depth of $\frac{1}{4}$ inch at each end, to secure an effective bearing length of 1 inch. The bearing load in pounds is thus numerically equal to the bearing pressure in pounds per square inch projected area.

Oil is carried to the bearing through a horizontal duct which intersects the bearing surface 135° from the crown on the "on" side. Labyrinth seals at each end of the bearing prevent escape of oil along the shaft, yet have clearance enough to cause no frictional torque. Oil escaping from the ends of the bearing is drained out of the end spaces by ducts which permit it to return to a sump by gravity.

Holes are also drilled through the housing into the tops of the end spaces, so that any desired gas can be passed out through the oil system and the labyrinth seals, thus permitting control of the atmosphere in contact with the oil.

Ring heaters (6) are clamped in grooves on each end of the housing; the housing temperature is controlled by a thermostat placed in a horizontal hole just below the bearing. A thermocouple is introduced into the top of the bearing in a hole drilled to within $\frac{1}{32}$ inch of the bearing surface. A continuous temperature record shows that the variation from the controlled temperature is rarely more than $\pm 2°$ F. An operating temperature of 250° F. was chosen for this work, in order to permit ready oxidation of the

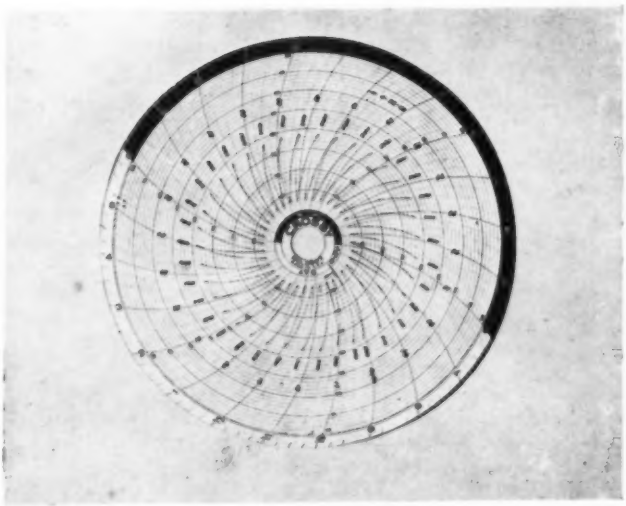

FIG. 2.

TYPICAL CHART SHOWING LOAD RECORD OVER 24-HOUR PERIOD.

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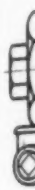

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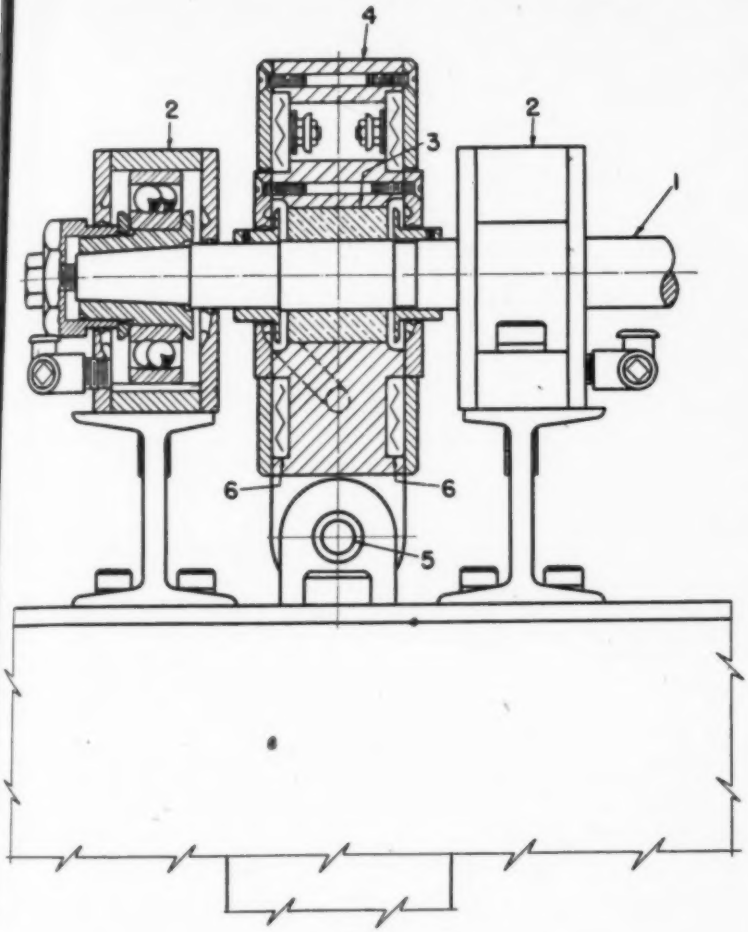


FIG. 3.

LONGITUDINAL SECTION THROUGH TEST BEARING AND HOUSING.

oil when exposed to air, to facilitate the temperature control by operating well above the point which the bearing would reach if no heat were added, and to reduce the lubricant viscosity so that excessive loading would not be required to enter the boundary region.

LUBRICATING SYSTEM.

The lubricating oil is contained in a large flask, from which it is lifted by a rotary pump having a capacity of 3 gallons per minute. The flask rests on

an electric heater, which is controlled by a thermostat over which the oil is drawn by the pump and which is set to maintain the oil at 250° F. Part of the output of the pump is returned directly to the sump from the pressure relief valve, which is set to maintain a feed pressure of 60 p.s.i. to the bearing. The remainder of the oil passes through a Whatman 43 × 123 mm. extraction thimble, and is then carried to a tee fitting placed as close to the bearing housing as possible. Oil from one branch of the tee enters the bearing at 40 p.s.i., and from the other passes through a by-pass valve and is returned to the sump. This is done in order to minimize cooling of the oil, which would occur to a considerable extent if only the small amount which is fed to the bearing were passed through the length of tubing necessary. With the exception of the bronze bearing, the only metal with which the oil comes into contact is steel. The sump is provided with a tube for passing any desired gas into the space above the oil. The space around the tubes entering the neck of the flask is tightly packed with cotton.

Procedure.

A new bearing and journal assembly was used for each run. The journal surface was ground and lapped to a fine finish and a nominal size of 1·0 inch. The bearing was then lapped to an inside diameter 0·001 inch greater than the journal. Measurements of the surface irregularity of both were made with a profilometer, and are shown in Table 1.

Table I.

Journal and Bearing Properties.

Journal Material: Nickel Steel S.A.E. No. 2340; Hardness, 415–440 Brinell.
Bushing Material: Sand-cast Bronze S.A.E. No. 64 (Cu 80%; Sn 10%; Pb 10%); Hardness, 65–80 Brinell.
Journal Speed: 107 r.p.m.

	Test #28.	Test #29.	Test #31.
1. Initial clearance (diametral)	0·001 inch	0·001 inch	0·001 inch
2. Final clearance (diametral)	0·0023 „	0·0025 „	0·0021 „
3. Original journal roughness (R.M.S.);			
Axially	5 micro inches	6 micro inches	4 micro inches
Circumferentially	5 „ „	6 „ „	3 „ „
4. Final journal roughness:			
Axially	6 „ „	8 „ „	10 „ „
Circumferentially	5 „ „	5 „ „	4 „ „
5. Initial bearing roughness:			
Axially	15 „ „	15 „ „	12 „ „
Circumferentially	15 „ „	15 „ „	12 „ „
6. Final bearing roughness:			
Axially	6 „ „	8 „ „	12 „ „
Circumferentially	6 „ „	6 „ „	6 „ „

Each oil sample was vacuum distilled to remove last traces of dissolved oxygen before use, and was transferred to the sump in an atmosphere of oxygen-free nitrogen. All parts of the system through which the oil flowed were first blown out with this nitrogen.

Mention may be made here of the great difficulty of obtaining a truly inert atmosphere. Commercial tank nitrogen, tried first, was wholly unsatisfactory. Even after this gas had been passed through a large furnace packed with copper turnings at cherry-red heat, the neutralization number of the oil rose nearly as rapidly as in free air. This commercial nitrogen contained only a minute fraction of a per cent. of oxygen. Finally some "pre-purified" grade nitrogen, such as is manufactured for filling incandescent lamps, was purchased; two consignments were used, and the second proved to be far superior to the first, as indicated by the stability of the neutralization number of the oil when this batch of nitrogen was employed.

Before each run the entire system was flushed by circulating several changes of solvent ($\frac{1}{3}$ ethyl alcohol, $\frac{1}{3}$ ethyl acetate, $\frac{1}{3}$ toluene) and by scouring the tubing with a test-tube brush.

The machine was started at room temperature; temperature was then slowly increased to 250° F. over a period of 20–30 hours, in order to prevent injury to the bearing due to distortion, and also to provide a running-in period.

Access of air to any of the exposed oil surfaces was prevented by applying the nitrogen blanket until the load at incipient seizure had reached a reasonably stable value. Some unexplainable variations generally occurred during this period, but they in no way obscured the later phenomena. Oxidation of the oil was usually secured merely by closing the valve on the nitrogen line, thus permitting air to diffuse into the system. In the case where an anti-oxidant was added to the oil, air was bubbled through the sump for some time. The periods during which the nitrogen blanket was applied can be seen in Figs. 6–10. Electrical heating was employed to avoid the possible contamination of the lubricant by combustion products of the heating gas used in earlier apparatus.

Small samples of the oil were withdrawn at frequent intervals for inspection analysis. Ordinarily, only viscosity and neutralization number were determined. In a few of the earlier runs more complete examinations were made.

Results.

As shown above, the data product of the machine comprises complete, continuously recorded load-time and torque-time charts; typical examples from one cycle of an actual run are illustrated in Fig. 4. The time scales of the two records are accurately synchronized, so that the load–torque curves may readily be constructed if desired. Practically, however, this is not necessary, because the loading is so nearly linear that the torque-time record may, for the purposes of the experiment, be considered identical with the load–torque curve.

In Fig. 5 is shown the relation between the coefficient of friction and the dimensionless variable ZN/P calculated from the data of Fig. 4. The minimum on this curve is conventionally taken as the condition of operation intermediate between thick and thin film types of lubrication. The curve is exhibited here to indicate the relative extents of the two regions in a typical cycle of the machine.

The principal interest in the results, however, lies not so much in the

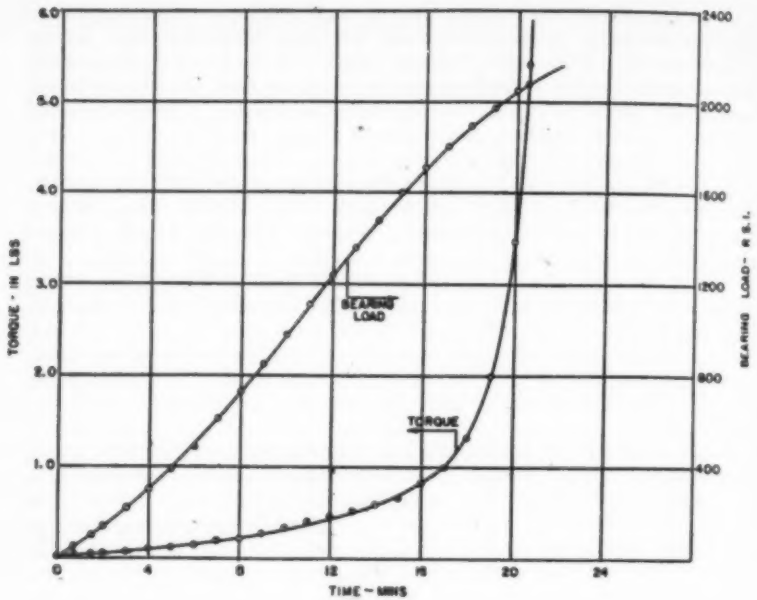


FIG. 4.

TYPICAL LOADING AND TORQUE CURVES (TEST NO. 31 AT 210 HRS.).

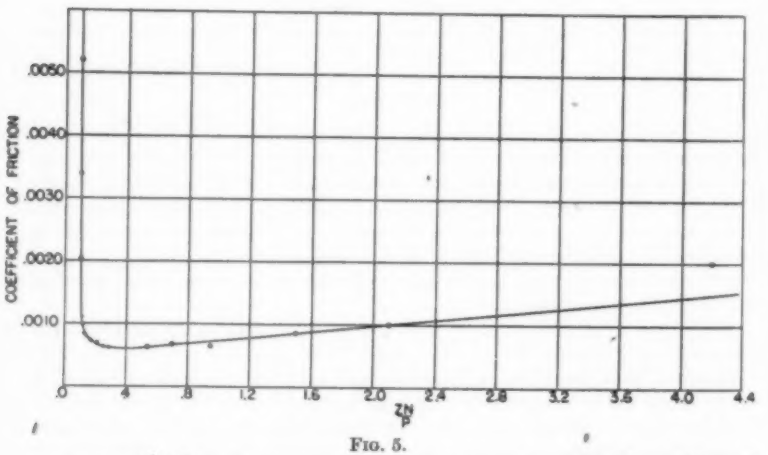


FIG. 5.

TYPICAL ZN/P VS. COEFFICIENT OF FRICTION CURVE (TEST NO. 31 AT 210 HRS.).

analysis of the data from single loading cycles, as in the change in the incipient seizure peaks of the cycles with the state of the lubricant. Five typical runs of this type are illustrated in Figs. 6–10, showing peak load and torque values, *i.e.*, incipient seizure values, together with other relevant data.

Results with a Paraffinic Oil.

Figs. 6 and 7 are duplicate runs on the same oil, a light, highly refined, paraffinic material; the inspection data for this oil are listed in Table II.

Table II.

Inspection Data for Paraffinic Oil.

Sp. Gr. : 0·8534.
Viscosity at 100° F. : 16·30 centistokes; Viscosity at 210° F. : 3·45 centistokes.
K.V.I. : 120.
Colour, N.P.A. : 1⁻.
Pour point : +10° F.
Flash point : 380° F.
Fire point : 420° F.
Carbon residue : 0·01%.
Ash : 0·00%.
Neut. number : 0·01.
Aniline point : 221° F.

The most striking phenomenon exhibited is the large increase of load-carrying capacity of the oil during oxidation, the value frequently becoming

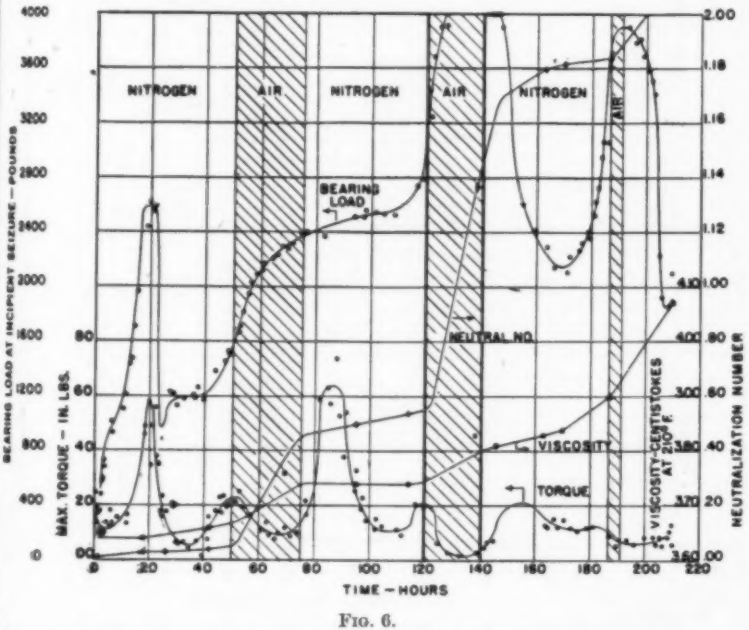


Fig. 6.

Effect of Oxidizing and Inert Atmospheres on the Performance of a Lubricating Oil.

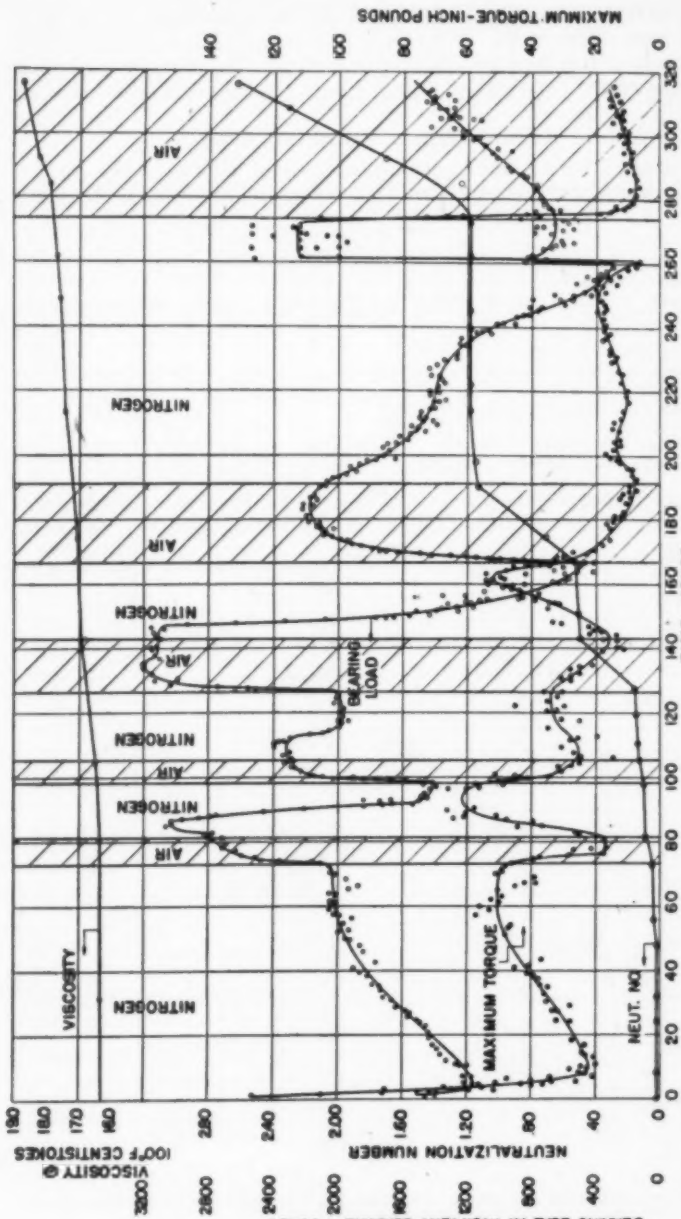


FIG. 7.

EFFECT OF OXIDIZING AND INERT ATMOSPHERES ON THE PERFORMANCE OF LUBRICATING OIL.

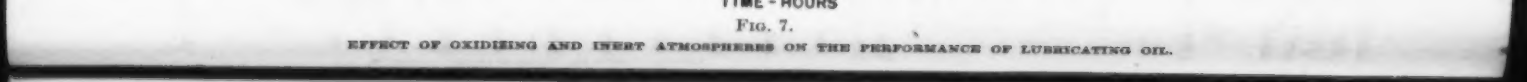
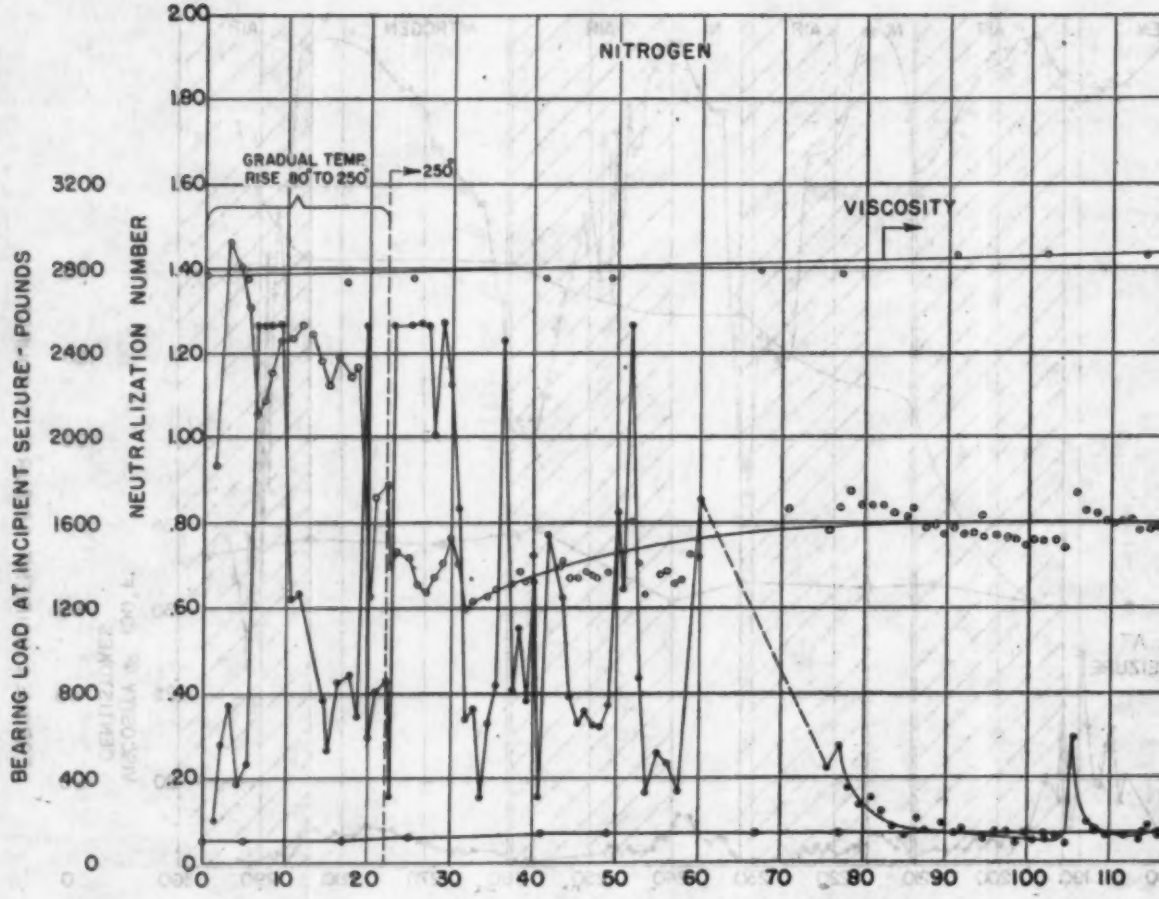


FIG. 7.

EFFECT OF OXIDISING AND INERT ATMOSPHERES ON THE PERFORMANCE OF LUBRICATING OIL.



EFFECT OF OXIDIZING

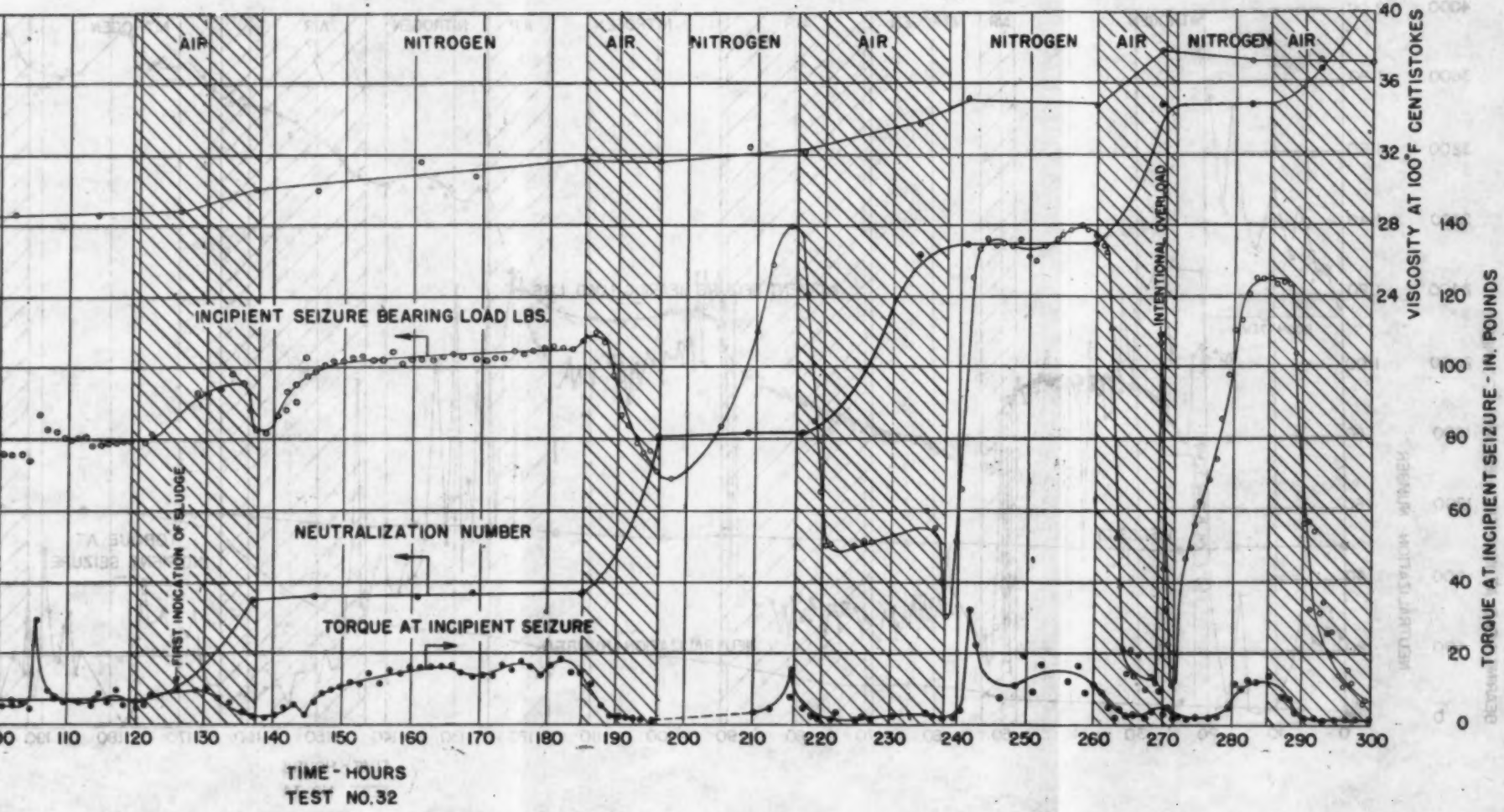


FIG. 8.

OF OXIDISING AND INERT ATMOSPHERES ON THE PERFORMANCE OF LUBRICATING OIL OF LOW V.I.

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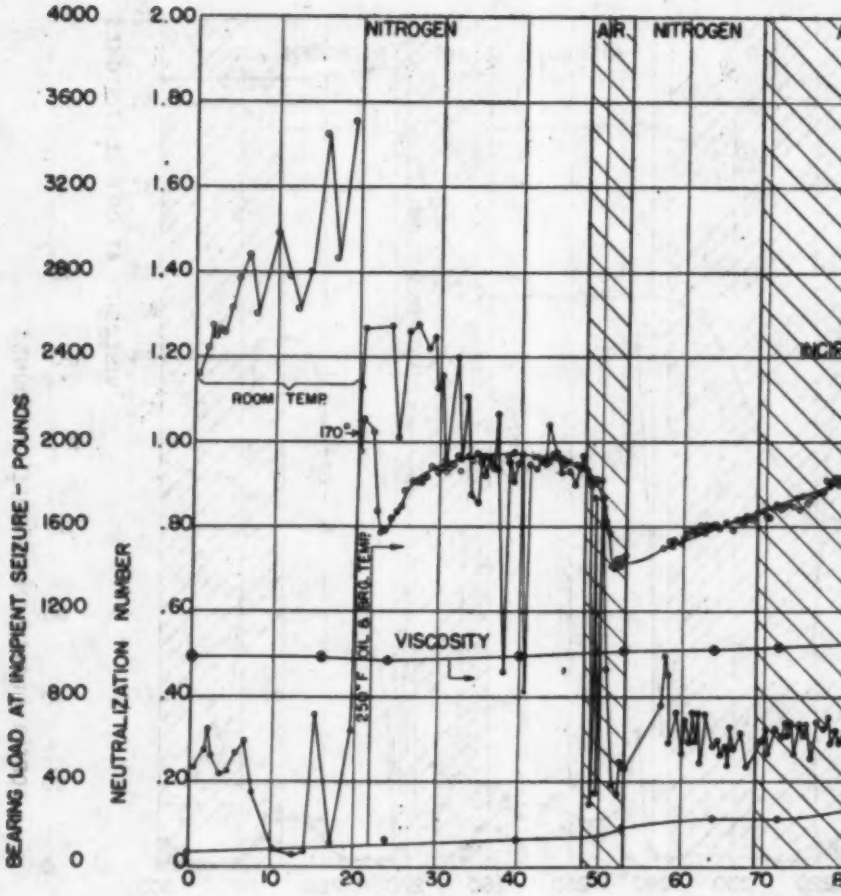

BEARING LOAD AT INCIPIENT SEIZURE - POUNDS
NEUTRALIZATION NUMBER
4000
3600
3200
2800
2400
2000
1600
1200
800
400
0
2.00
1.80
1.60
1.40
1.20
1.00
.80
.60
.40
.20
0
NITROGEN
AIR
NITROGEN
ROOM TEMP.
170°
VISCOSITY
0
10
20
30
40
50
60
70

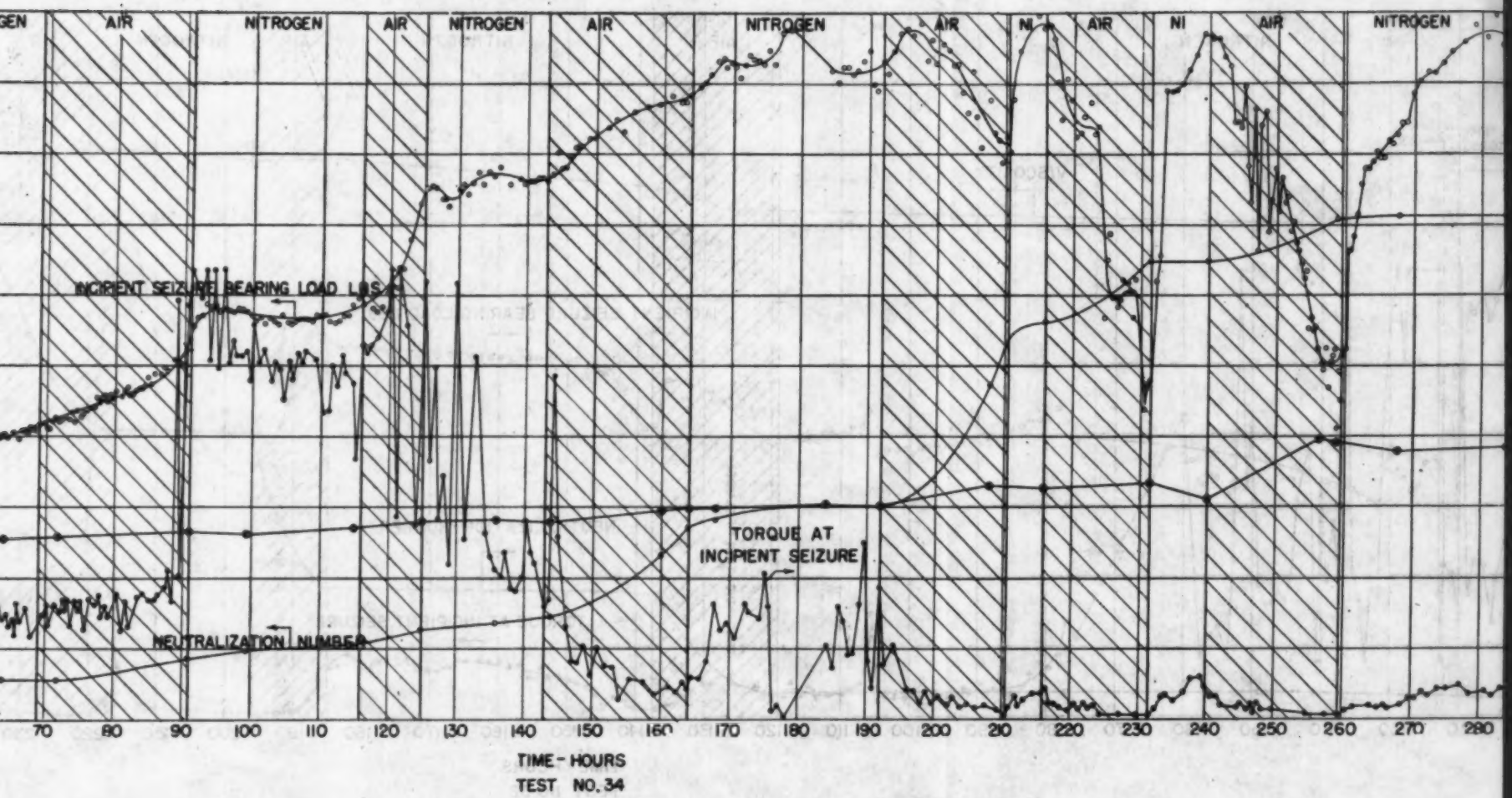


FIG. 9.

EFFECT OF OXIDIZING AND INERT ATMOSPHERES ON THE PERFORMANCE OF LUBRICATING OIL OF LOW V.I.

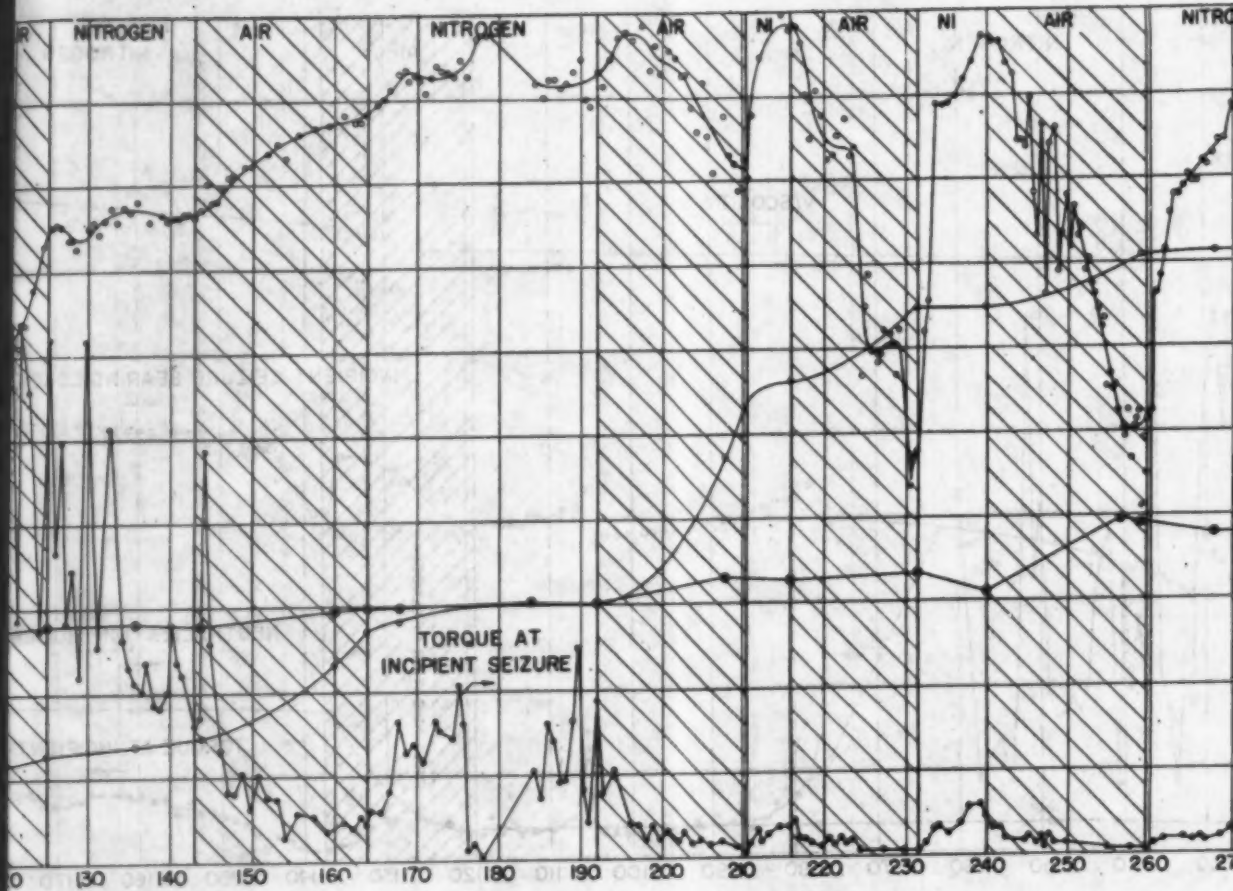
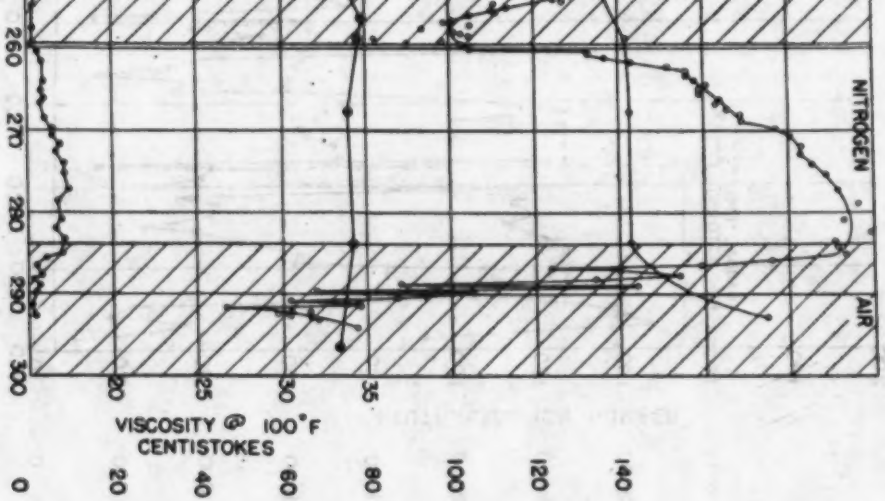


FIG. 9.

INERT ATMOSPHERES ON THE PERFORMANCE OF LUBRICATING OIL OF LOW V.I.


NITROGEN
AIR
260
270
280
290
300
20
25
30
35
VISCOSITY @ 100°F
CENTISTOKES
0
20
40
60
80
100
120
140
TORQUE @ INCIPIENT SEIZURE - IN-POUNDS

[To face p. 303.

twice that of the unoxidized oil. Even more remarkable is the indication that the effect is temporary; displacement of the oxidizing air with an inert nitrogen blanket causes the seizure load to decrease to near its value before oxidation, in some cases to even less than that amount. The more extensively the oil is oxidized, the longer is the time required for the return, but the effect is observed quite as strongly.

Apparently certain of the initial oxidation products of the oil act as agents which delay incipient seizure, probably by being strongly adsorbed on the bearing surfaces. These materials may, however, be unstable under the conditions of the experiment, and undergo change into less beneficial compounds, or are rendered inactive in some manner. The gain in load-carrying capacity for a given air phase of the atmosphere cycle will tend to increase as the run proceeds. This may be partly due to the regeneration of the beneficial compounds from the intermediates to which they had reverted in the absence of oxygen, together with the continued oxidation of the unoxidised oil; this would result in a steady increase in the concentration of the beneficial compounds. A marked gain in the response occurs with the initial precipitation of insoluble material in the sump. This is discussed below in connection with related phenomena observed in the case of a naphthenic oil.

Results with Naphthenic Oils.

Figs. 8 and 9 illustrate the results obtained with a typical naphthenic oil of low viscosity index; the inspection data for this oil are given in Table III. The figures show that during the early part of each run this oil

Table III.

Inspection Data for Naphthenic Oil.

Sp. gr.: 0·9230.
Viscosity at 100° F.: 27·69 centistokes; Viscosity at 210° F.: 4·06 centistokes.
K.V.I.: 29.
Colour, N.P.A.: 2+.
Pour point: −30° F.
Flash point: 310° F.
Fire point: 350° F.
Carbon residue: 0·01%.
Ash: 0·01%.
Neut. number: 0·03.
Aniline point: 309° F.
Steam emulsion number, sec.: 86.
Refractive index, n_D^{20} C.: 1·5078.
Sulphur: 0·24%.
Naphtha insol., mg./10 g.: 0·7.

behaved much as did the paraffinic product; seizure load rose slightly and slowly with exposure to the oxygen of the air, and decreased each time the air was blanketed out by nitrogen.

In that portion of the test, however, following initial precipitation of sludge, the effects were reversed. The seizure load now decreased when air was admitted and rose when it was excluded. The reason for this is not clear. A possible explanation may be found in postulating the deposition of a sticky layer of insoluble oxidation products which exhibit a specifically different friction behaviour. When air is excluded, the formation of these products ceases and they are worn off the bearing surface

mechanically; this allows the seizure load to increase toward its original value.

This phenomenon is in marked contrast with that pointed out above for a paraffinic oil. In that case, precipitation of insoluble material was accompanied by a marked increase in seizure load. Again, a possible explanation may lie in a postulated difference in the character of the insoluble material precipitated on oxidation from the one type of oil and the other. It is strongly suspected that the first precipitates from an oxidized paraffinic oil are of soap type and those from a naphthenic oil of asphaltene type. The soap-type precipitate either does not adhere to the metal surfaces or does not decrease seizure load. The formation of soaps should, it can be assumed, be preceded by the formation of soap-forming acids; such compounds are known to decrease coefficient of friction. On the other hand, the asphaltene oxidation product of a naphthenic oil, if deposited on the bearing surface, might serve to decrease seizure load.

TABLE IV.

Results of Comparative Tests on Seizure Load, or Load-Carrying Capacity of Some Commercial Oils.

Tests run in nitrogen in the order below on the same bearing.

Order of Test.	Oil.	Seizure Load (pounds).		
		Minimum.	Average.	Maximum.
1	A	1812	2248	2520
2	B	765	1631	2737
3	C	1197	1487	1937
4	D	1075	1275	1443
5	E	1168	1470	1675
6	B *	1380	1646	2452
7	A *	1692	1991	2327
8	F	1745	2080	2522
9	G	1493	1573	1660

* Duplicate tests.

Note.—Operating temperature was adjusted to equalize viscosity of all oils, to obtain an absolute viscosity of 3·88 centipoises. Temperature range 261–275° F.

The above explanation may agree with the possibility that the oxidation products of a paraffinic oil would be more polar than those from a naphthenic oil.

In order to obtain an indirect confirmation of the influence of oxidation on seizure load, a run was made in which 1 per cent. of a proprietary inhibitor was added to the low viscosity index naphthenic oil. The results are shown in Fig. 10. The inhibitor is believed to have anti-oxidant and detergent properties. It will be seen that the seizure load, except for the run-in period, remained quite constant for almost 200 hours, irrespective of the atmosphere to which the oil was exposed.

The torque data as a whole were far more erratic than the seizure data collected in the runs, particularly as regards the peak values. It must be borne in mind here that *seizure*, in the sense used throughout this paper, is really incipient seizure, the state at which the rate of increase of torque

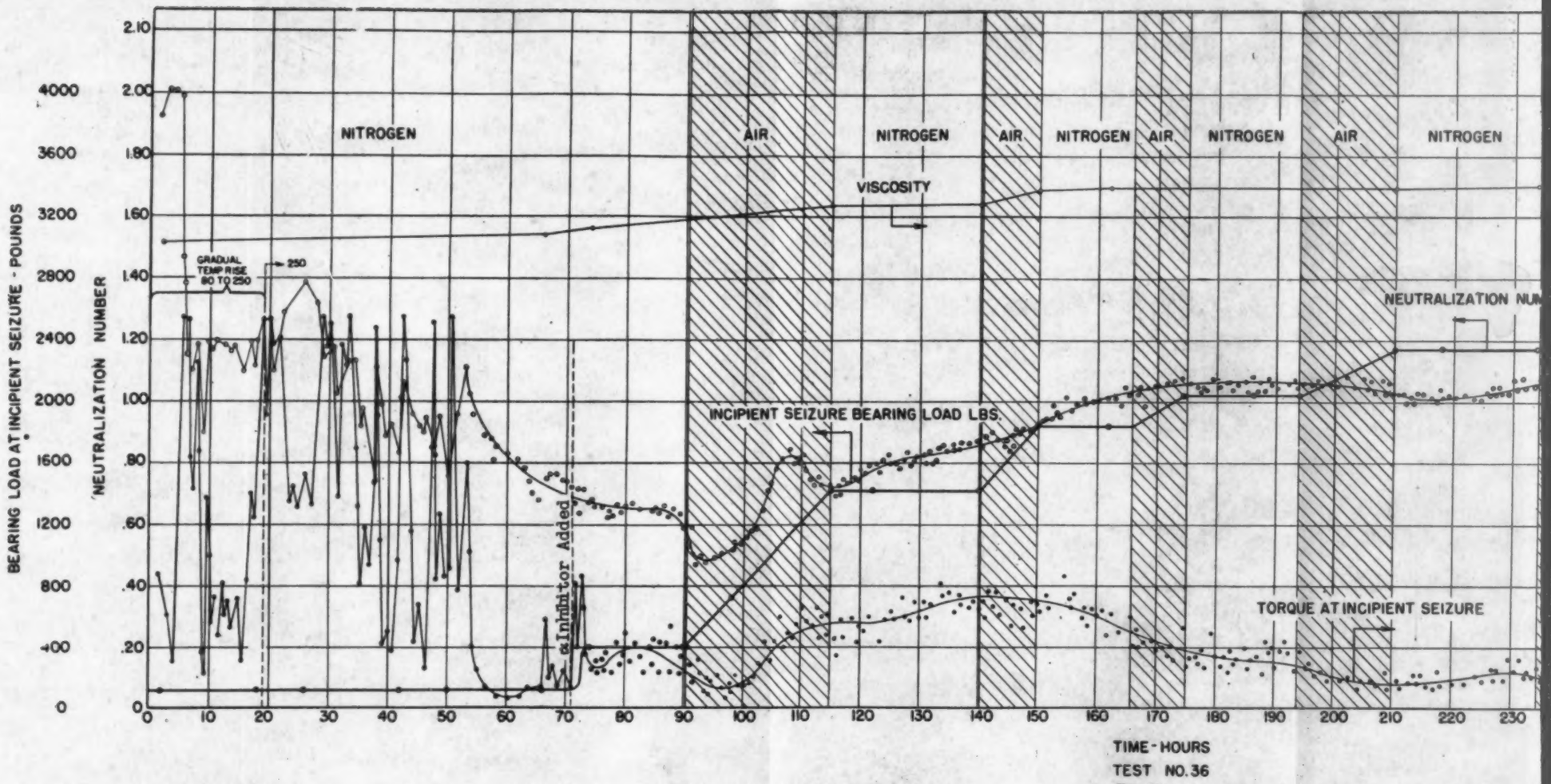


FIG. 10.

EFFECT OF OXIDIZING AND INERT ATMOSPHERES ON THE PERFORMANCE OF LUBRICATING OIL OF LOW V.I. + 1% INHIBITOR.

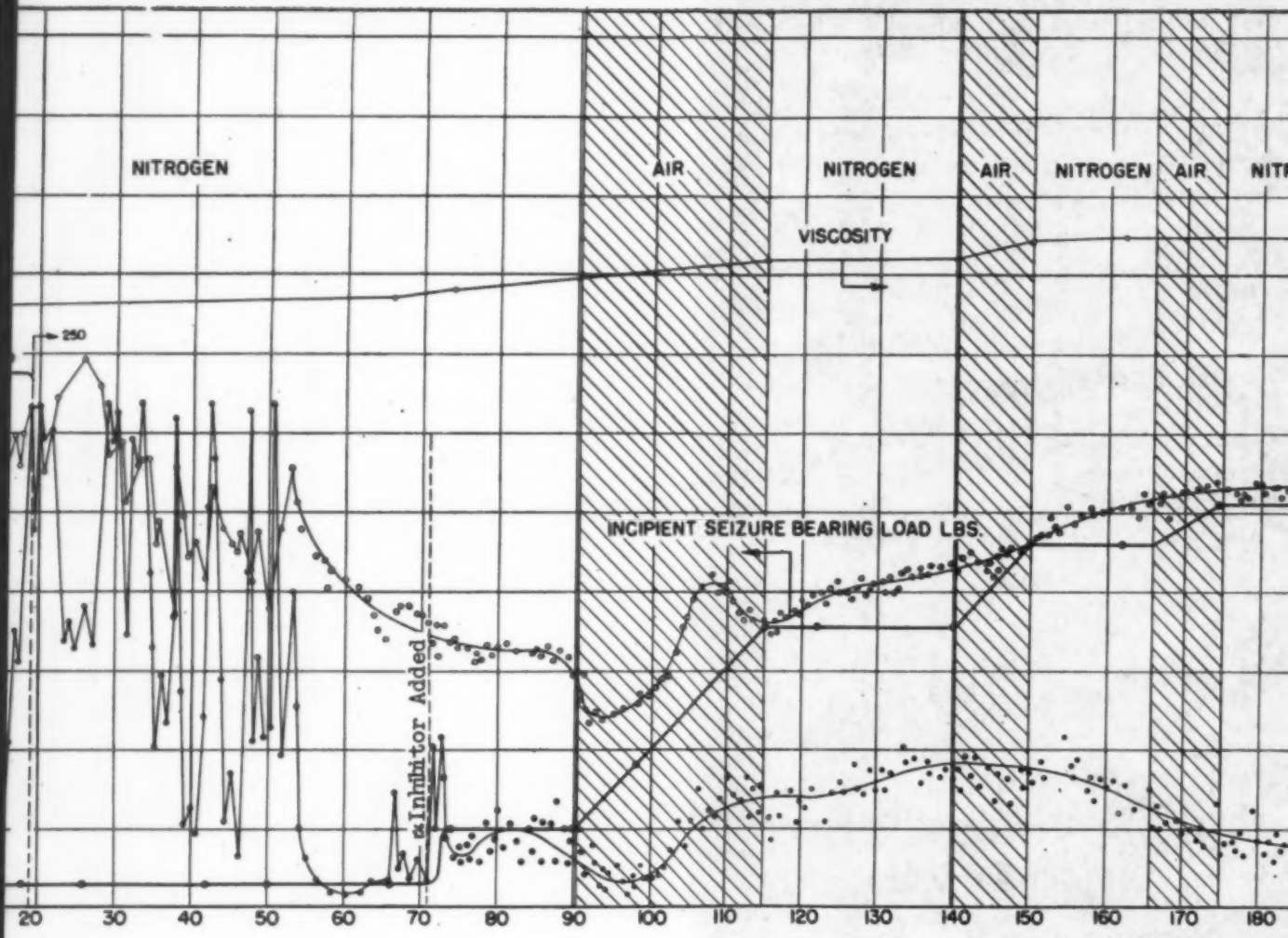
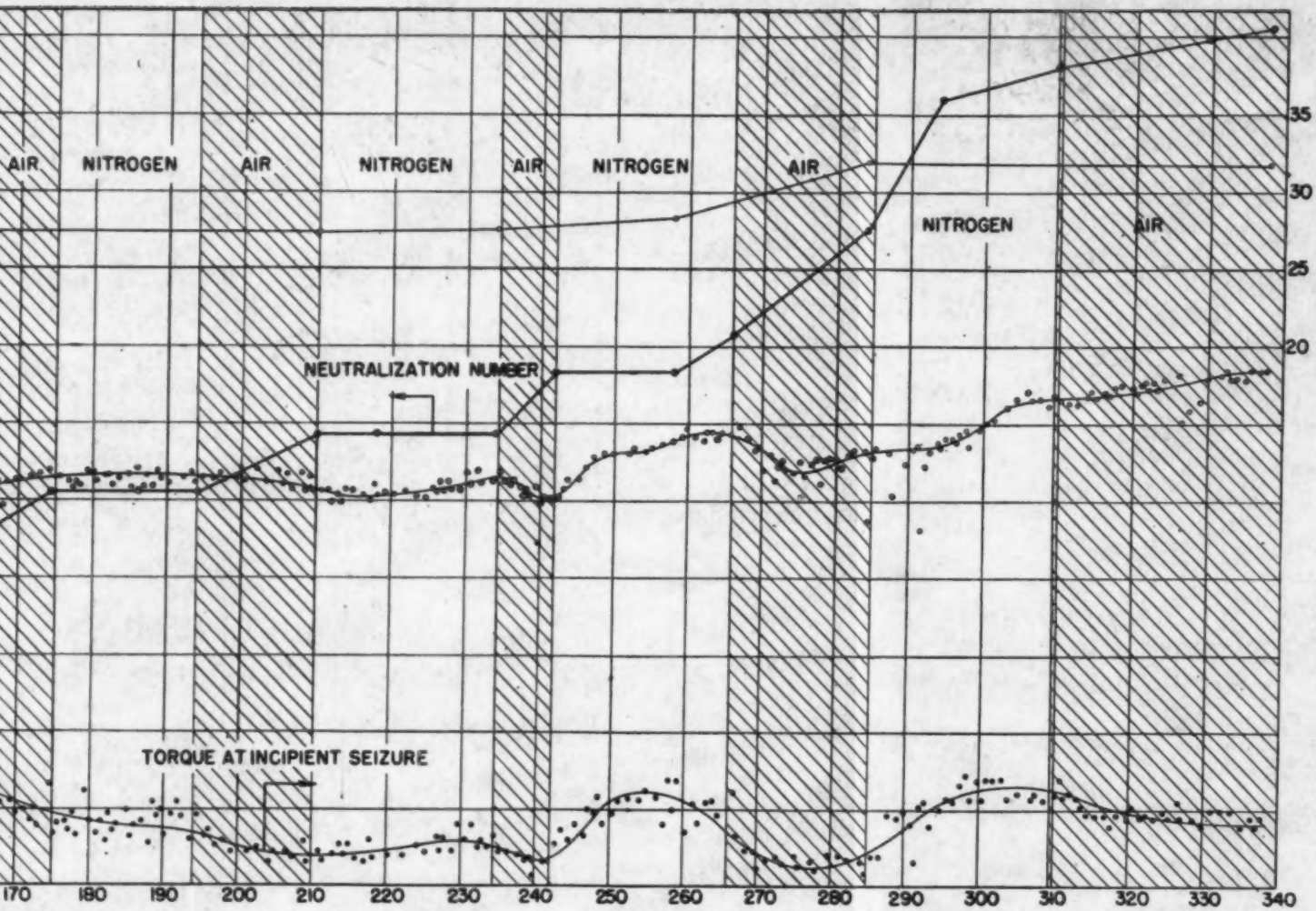


FIG. 10.

EFFECT OF OXIDIZING AND INERT ATMOSPHERES ON THE PERFORMANCE OF



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10.

FORMANCE OF LUBRICATING OIL OF LOW V.I. + 1% INHIBITOR.

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becomes large enough over a sufficient time to trip the breakdown mechanism of the machine. Experience has shown that this represents a condition very near actual seizure, when, of course, the torque becomes infinite.

Even considering the nature of the "maximum torque," the results are difficult to explain. No definite correlation exists between it and the maximum load, even though the two generally increase and decrease together. Isolated cases have been observed where the torque maxima for consecutive cycles are of different orders of magnitude, while the seizure load remained unchanged. Occasionally the torque increased as the seizure load decreased. Much more data are required before conclusions can be drawn or hypotheses formed.

To permit orientation of these results with current practice, Table IV shows the results of comparative tests on seizure load of some commercial S.A.E. 20 oils. These tests were run in nitrogen alone, lasted only about 15 hours, and all used the same bearing. A control run, of about 4 hours, was made between each of the tests, using a different sample of the same oil for each. Following each run the system was cleaned by circulating the solvent used for flushing in the previously described tests. These frequently showed high or low values at the beginning, but soon approached the initial value for the reference oil, indicating that the machine had returned to its original condition. Following the test of a drastically "doped" oil, no satisfactory control values could be obtained, probably because of a change in the nature of the bearing surfaces.

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THE INSTITUTE OF PETROLEUM

A MEETING of the Institute was held at the Royal Society of Arts, John Adam Street, Adelphi, London, W.C.2, on Thursday, 25th March, 1943, Mr. C. Dalley, President, occupying the Chair.

A discussion on the subject of "Petroleum as a Source of Synthetic Materials" was opened by Dr. A. E. Dunstan, Professor F. H. Garner, and Mr. J. A. Oriel, M.C.

DISCUSSION.

DR. A. E. DUNSTAN, before opening the discussion, said that the Council of the Institute was doing its best to continue the monthly meetings, and he urged Fellows and Members to provide more material for the *Journal*. Good papers and other material for publication were very much needed, in order to keep the Institute not merely alive, but flourishing.

The subject of the discussion on the present occasion was, in effect, the production of material from the basic products of the degradation of petroleum.

Some years ago he had invented the expression "petroleum bricks" and had raised the question of how to obtain them and what to build with them. No one in these days who read the literature on the subject could fail to realize that those petroleum bricks were a very real entity in modern chemical affairs. Those who were engaged in the oil industry to-day were inclined not to have too much regard for what had happened in the past, but those happenings had built up the present structure, and he proposed to deal for a few moments with the history of the subject.

The first utilization of petroleum bricks had probably been brought about by the revered founder of the Institute, Sir Boverton Redwood, many years ago, when he and the late Sir James Dewar had achieved the cracking of petroleum. The word "cracking" was perhaps inappropriate; what really happened was that, by the impact of high temperature, heavy oils were split or broken down into bricks. With those bricks, at that very early stage, long before the last war, Redwood and Dewar had inadvertently built up aromatic hydrocarbons.

He had had the good fortune, a quarter of a century ago, to be associated with the late Professor Wheeler in attempting to go a stage further than Redwood and Dewar had gone, and they had been able to show that from the ordinary, plain, recalcitrant hydrocarbon, methane, aromatic hydrocarbons could be produced. They had been able to show that, by the impact of temperatures of the order of 1000° C., 1000 cubic feet of methane, for example, would give 1½ gallons of liquid, and that that liquid was in effect quite similar to coal tar. It was a somewhat curious fact that one could start with coal, petroleum, straw, or wood, and, given the temperature, could obtain almost the same products. A "coal" tar could be obtained from all those starting-out materials if the temperature was sufficiently high.

He thought it must be assumed that, in the long run, one came down to the ultimate radicals associated with the thermal decomposition of hydrocarbons; to CH, CH_2, and CH_3, and those radicals really were the bricks with which the present meeting was concerned. The very early work carried out showed that from those simple radicals complicated structures could be built up. With those simple bricks houses and edifices could be built, and he would like to direct attention to some of those edifices: plastics, synthetic rubber, solvents, and so forth.

The point that he wished to emphasize was that petroleum had ceased to be a simple crude raw material for half a dozen every-day products; it had ceased to be a raw material for kerosine, gasoline, gas oil, lubricating oil, bitumen, and so forth. It had begun to resemble coal tar a hundred years ago; it had begun to be the fount of starting-out materials for the whole range of synthetic chemistry. That was admittedly a very big claim to make, but assuredly the present members of the Institute would see the time when coal tar would take a second place in the development of the great industries now in their infancy.

It would be remembered that cracking began to be a serious problem because of the demand for more and more liquid motor spirit. It was not a question of quality then,

but a question of quantity. It was not possible, twenty-five years ago, to obtain a sufficient amount of motor spirit from crude oil by direct distillation to cope with the demand unless a vast amount of ancillary products were produced for which there was no particular need, such as kerosines, gas oils, and heavy residues. A little later on the question of quality arose, and cracking became a process for the vast improvement of performance in the engine as compared with the performance of the straight-run material. The United Nations would have been in a very unfortunate position to-day had they been dependent on straight-run gasoline from ordinary crude oils. The question of quality became super-important, so much so that straight-run gasoline had to be cracked to obtain the super-characteristics demanded by the engine. That necessarily brought about the production of greater and greater quantities of by-products, so that one had to contemplate, in drastic thermal treatment, that a third of the initial oil would come out in the form of hydrocarbon gases. Therefore the industry, having to provide super-quality, had to produce a vast amount of material which in effect was the new material for a great new series of industries.

He did not propose to deal in great detail with the subject under discussion at the present meeting, but rather to open a debate, which he hoped would be very profitable, on the developments which were likely to occur in the very near future in the building up of structures. Professor Garner and Mr. Oriel would deal at much greater length than he could with these obvious developments of applied science, but he would wish to mention one or two somewhat striking examples which had occurred in the last few years.

He would refer first to the building up of *iso*-octane from the butenes. Not very many years ago butene, like methane and the rest of the lower hydrocarbon gases, was indeed a waste product, but, based on the pioneer organic chemistry of Butlerow and Ipatieff, it was shown that the butenes were capable of polymerization and that from two molecules of *iso*butene one could build up an octene with the 2 : 2 : 4-trimethylpentene structure, and from that particular octene, by simple hydrogenation, *iso*-octane could be derived. That was the starting-point, from the point of view of the petroleum industry, of all modern development in the chemistry of the lower hydrocarbons.

He could remember very well a meeting in Chicago, about fifteen or sixteen years ago, at which Graham Edgar first announced his scheme for the comparison of liquid fuels for the automobile engine, when he indicated, for example, that the substance of poorest performance was *n*-heptane, which he obtained by the distillation of certain resins from the Californian pine, and that the best of all was *iso*-octane, produced then in the laboratory by somewhat difficult methods. Those two substances, *iso*-octane and *n*-heptane, were fixed as the standards of performance not very many years ago.

It was astonishing how in the meantime the organic chemist had solved the problem of the utilization of the lower hydrocarbons. Month by month advances had been made in the application of those substances to synthetic treatment, and he would like to remind members of one or two of them.

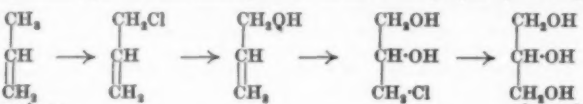
If one wanted to make *iso*-octane to-day, the starting-up materials were an olefine and a C_4 *iso*paraffin, *iso*butane, and any of the butenes; in fact, *iso*butane and the propenes or the ethylenes. *iso*Butane was essential for the purpose, but there was a deficit of it. Natural petroleum did not produce the quantity that the chemist wanted. He had often contemplated the extraordinary lack of foresight in Nature's Chemistry. One would have thought that Nature would have foreseen all the present difficulties and have produced *iso*butane in place of *n*-butane, but that had not been the case, so to-day it was necessary to make *iso*butane for synthesizing the C_8 hydrocarbons. By a process of isomerization, *n*-butane could be converted into *iso*butane, and in turn the *iso*butane could be converted into high-anti-knock materials. He had often thought that the reaction of the *iso*paraffins with the *n*-olefines or the *iso*-olefines was one of the prettiest in the organic chemistry of petroleum. The simple reaction of the tertiary carbon atom of the *iso*paraffin with the alkenes was outstanding in its importance in the industry. He remembered talking some years ago to Ipatieff, who had been a pioneer in this sort of work, and in the course of conversation they arrived at the somewhat fundamental point that the tertiary carbon atoms in *iso*butane were not very dissimilar from the tertiary carbon atoms in the aromatic series. Ipatieff had at one time been concerned with the addition of ethylene to benzene, and one of the tertiary carbon atoms in the benzene ring took up ethylene under the influence of a catalyst and ethylbenzene was formed. It was a natural development of that work to

discover that *iso*butane reacted very similarly with the butenes, under the impact of an effective catalyst, to produce the 8-membered structures, the *iso*-octanes.

Another point had arisen which he thought would seem reasonably obvious to the chemists who were present. It was well known that the aromatic hydrocarbons had properties which the straight-chain hydrocarbons did not possess; they were very much superior in engine performance from the standpoint of their oxidation reactions. When the organic chemist contemplated the difference between ordinary straight *n*-heptane and toluene, it might have raised in his mind a great many possibilities and problems. For instance, how could a substance like *n*-heptane, which from the point of view of the chemical industry was a comparatively useless substance and from the point of view of the petroleum industry was useless as a motor fuel, be got into ring structure; in other words, into toluene? Therefore, with the effort to build up the chemical bricks into high-anti-knock bodies of the *iso*-octane type, a parallel set of researches was made to build them up into ring structure, into materials such as benzene, toluene, and so forth, and hence arose the modern development of cyclization, in which the straight-chain hydrocarbons bent round into ring structure, with loss of hydrogen and then with still further loss of hydrogen, right into the aromatic derivative; in other words, from *n*-heptane into toluene.

It would therefore be seen that the impact of organic chemistry on the petroleum industry, with its development of exceedingly high-anti-knock material, and the transformation of straight-chain paraffins into *cyclo*paraffins, and *cyclo*paraffins into aromatic hydrocarbons, had gone steadily on, but there were many other aspects which must not be disregarded.

He was inclined to think that one of the most delightful examples of the impact of plain organic chemistry on the petroleum industry was the work of E. C. Williams in synthesizing glycerol from propylene. Starting with propylene, allyl chloride was obtained by the addition of the halogen. Hydrolysis led to allyl alcohol which, on hydrochlorination, yielded the chlorhydrin, and this readily hydrolysed to glycerol.



propylene glycerol

As Williams had very truly said, this synthesis would be a curb on any great increase in the price of the natural glycerol derived from fats.

He had referred to the impact of temperature on the lower hydrocarbons and had mentioned the work he had done with Professor Wheeler in producing aromatic hydrocarbons from methane. Fig. 11 in "Chemistry and the Petroleum Industry," by Dr. A. E. Dunstan, *J. Inst. Petrol.*, July 1943, **29** (235), 163, showed a modern pyrolysis plant. Actually the plant did not use methane, but surplus lower hydrocarbon gases under the impact of temperature and pressure were processed, producing material of a high aromatic content.

The most important aspect of the new synthetic chemistry was the development of catalysis. Fig 13 in *loc. cit.* showed a simple unit in which the lower hydrocarbon olefines, ethylene, propylene, butylene, and so forth, were subjected to the influence of a contact medium. Under the impact of catalysis the lower hydrocarbon olefines united and built up aggregates; C_2 became C_4 and C_3 became C_9. From what was at one time a waste product a building-up material of great value had been found.

Prof. F. H. Garner said that when the present meeting was arranged it was proposed that those who opened the discussion should spend only a few minutes in introducing the subject; in fact, they were merely to provide an opportunity for discussion. He had prepared a very short note on the subject of synthetic rubber.

The most important individual product synthesized from petroleum would appear to be synthetic rubber, although *iso*-octanes for the manufacture of aviation gasolines would come as a close second. The task of making synthetic rubber—Buna S, Butyl Hycar, Neoprene, and Thiokol—would again appear to be one of the most formidable manufacturing tasks in the present war, and one of the most important from the point of view of winning the war.

According to the Baruch Committee, which it would be remembered was appointed by President Roosevelt to give a decision on some of the rubber problems in the United States, an overall production of 850,000 tons of Buna S, 130,000 tons of Butyl rubber, 70,000 tons of Neoprene, and 60,000 tons of Thiokol were required. Buna S was made by co-polymerizing butadiene and styrene, Butyl rubber was made by co-polymerizing butylene and a diene, Neoprene was made from chloroprene, which was the chlorinated butadiene, and Thiokol was made from sodium polysulphide and ethylene dichloride. All the amount required would not be made from petroleum, as of the butadiene for the manufacture of Buna S about 240,000 tons were to be made from grain alcohol which was available. The programme for the manufacture of butadiene had to be very carefully co-ordinated with the programme for the manufacture of butylenes for the *iso*-octane manufacture in aviation gasoline production, and there had apparently been some conflict in the steel requirements, *i.e.*, in the requirements of steel for the manufacture of the plants, although the Baruch Committee had considered that the conflict need not be serious.

The very large requirement of the C_4 fractions for the manufacture of Buna was originally based on butanes, which, of course, were available in large amounts in natural gas and also in cracked gases and other gases from refineries, but it was soon seen that the plants for the manufacture of butylenes from butane (an intermediate step in the manufacture of butadiene) would require too much steel. Attention was therefore concentrated on cracking operations which would give large proportions of butylenes, and modifications of known cracking processes and developments of new processes followed, amongst which the Fluid Catalyst Process and the Houdry Process were particularly important.

For the conversion of butylene and butylene–butane mixtures into butadiene, some 280,000 tons were said in November last to be in process of construction or planned, and some 110,000 tons by direct thermal cracking of mixed petroleum hydrocarbons. A new Houdry process was introduced in the meantime for the cracking of butane directly into butadiene, with yields claimed to be as large as 67 per cent., and an additional 60,000 tons had been agreed, making a total of 420,000 tons of butadiene from petroleum. In addition to that quantity, another 100,000 tons was contemplated from a group of small companies participating in a refinery conversion programme.

In addition, styrene was required in the proportion of about one part to three parts of butadiene, and some of that might be made from ethylene derived from petroleum.

The yield of Buna was 1·1 long tons from 1 short ton of butadiene. It was rather interesting that co-polymerizing capacity was based on long tons, that being the normal method of expressing weight of rubber, and that butadiene and butylene production was based on the short ton of 2000 lb.

This programme appeared to be the most important ever undertaken in the petroleum industry, and was based on the extensive research work carried out in the various petroleum companies' laboratories in recent years, which had been applied to full-scale manufacture under the extreme stress of war conditions.

Mr. J. A. Oriel said it was a terrifying prospect for him to try to say anything on the subject of the discussion, following as he did the greatest expositor on petroleum chemistry in the country and a professional professor of the subject, but, as the third and junior member of the trinity (he hoped he would be allowed to call it a trinity without any invidious comparisons being made by the audience), he was left to deal with the odds and ends on which the two previous speakers had not touched. He was sure everyone must be wondering what there was left for him to deal with, and he himself was wondering about that. He had been told by Dr. Dunstan that he was to speak for only about ten minutes, as many of the members present would wish to speak on the subject of the chemistry of petroleum.

Dr. Dunstan and Professor Garner had dealt very clearly with what he might call the chemistry side of petroleum as distinct from its fuel side, and Dr. Dunstan had made quite clear the development of the use of the chemical activity of the olefines from cracked gases, so that he himself was left not so much to deal with the chemistry of petroleum as to fill in a few gaps on chemicals derived from petroleum. It was a little difficult to do that without laying himself open to the criticism that he was merely giving a catalogue of the chemicals which could be derived from petroleum, but he would try to avoid doing that, and would merely mention a few things, so as to provoke

a certain amount of discussion on those products. He was sure that some great man had said at some time or other that the subject of a lecture could be made to mean whatever one wanted it to mean, and he was going to take advantage of that on the present occasion.

Some people had wandered from the path of pure chemistry in the course of their association with the petroleum industry, and had become more concerned with the chemical engineering side than with the purely chemical side, and the subjects which Dr. Dunstan had introduced in his address had become rather terrifying to them. In his youth it had been the custom to deal with such things as methane, ethane, and propane, and to dismiss everything else as higher homologues, and those were the substances, he thought, which it was now necessary to look into much more closely. Therefore he would prefer to go back for a few minutes to certain somewhat heterogeneous mixtures, rather than to deal with the pure chemicals which could be built up of Dr. Dunstan's bricks.

Before doing so, he wished to refer to one or two interesting chemicals that were not usually mentioned; they were not chemical compounds, but were elements of great importance which were derived from petroleum. The first and most obvious of those was carbon black, which was formed by the incomplete combustion of petroleum gases and by the rapid cooling of those gases. It was very important during the war to realize the contribution that carbon black had made to the rubber industry. The bulk of the carbon black was incorporated in the production of rubber tyres, and that incorporation increased the life of tyres from about 4000 or 5000 miles to 20,000 or 30,000 miles. It was very interesting to see how the petroleum industry had come to the aid of the internal-combustion engine industry, not only in the provision of fuel, of which it was the main source, but also in the provision of material for tyres.

Another element which was of interest in the petroleum industry was helium. It was not often that attention was directed to the fact that the petroleum industry was the main source of that element, but it was so. All the members were familiar with the use which had been made of helium in airships, owing to its low density, lightness (it was the next lightest element to hydrogen) and safety. The fact that the petroleum industry in America was responsible for the production of the bulk of the helium had in the past almost led to international complications. It was interesting to note that the largest production of helium outside the United States, which was from a spring in Alsace, would provide helium only at such a rate that it would take 1400 years to fill a Graf Zeppelin. The pre-war implications o that were, he thought, obvious. Helium, however, had been used recently in a much more interesting way—namely, in connection with diving. The trouble known as "divers bends," which was a serious matter, was brought about when divers had been down to 200 or 300 feet and were then brought up too suddenly; it was due to the solution of nitrogen from the air in the blood and the sudden release of it. The bubbles, pressing on nerve centres, brought about very unpleasant results, which caused convulsions and sometimes death. It was found that helium, being much less soluble than hydrogen in water, could be supplied to the divers as helium air instead of nitrogen air, and would get rid of that trouble. Not only were men able to go down to greater depths and to carry out more work when they were down there, but the unpleasant results which had formerly been experienced were completely abolished. The first time helium was used in this connection was in saving the lives of several men on the American submarine *Squalus* in 1939. Helium was so often mentioned in connection with airships and its use as a life-destroying agent that he thought he would like to mention its use as a life-saving agent.

Having dealt with those two elements, carbon black and helium, he proposed to refer briefly to some of the more intricate mixtures, with which those engaged in the petroleum industry were much more conversant than they were with normal pure compounds, and he wished to refer first to plastics.

The coal-tar industry had contributed, up to the present, a great deal more raw material to the plastic industry than had been contributed by the petroleum industry, but, as was obvious from what Dr. Dunstan had already said, there were in the petroleum industry very many good starting-points for plastics. The coal-tar industry at present accounted for about 70 per cent. of the raw material for plastics, 15 per cent. coming from cellulose and the remaining 15 per cent. being other raw materials, in which were included the raw materials from petroleum. During the war period the

petroleum industry was devoting a great deal more attention to the production of synthetic rubber than to plastics, but unquestionably when peace came again the industry would be able to turn its attention more actively to the production of plastics, and there would be a great deal of equipment available in the refineries to turn over to that very great industry.

The plastic industry was not a very old one, being about the same age as the chemical industry based on petroleum. With all due respect to Dr. Dunstan, the real building up of the bricks that he had mentioned had been done at refineries during the last fifteen or twenty years, and the plastic industry had been in existence for about the same length of time. He did not suggest that the chemistry of the high polymers had been known for only that short time, but he thought it was only within that time that it had been found possible to elucidate the molecular structure of the high polymers and to prepare them in the laboratory and the plant. The some point had been reached in the polymer industry as had been reached in many other industries, and it was very characteristic of chemical development. An attempt had been made to imitate nature in the production of a naturally occurring product, and now, with further knowledge of the product itself and its chemical composition, the point had been reached when it was possible not only to imitate nature, but to improve on it and to find similar but different materials with special uses which had not been even imagined when the investigation was first undertaken.

Without generalizing too much, he thought it could be said that a high polymer which consisted of a chain which fitted badly into a lattice shape and would tend to return to its normal shape gave synthetic rubber, a high polymer which fitted easily into a lattice structure gave fibrous materials, and the high polymers which were in between those two types gave plastics, and therefore were quite closely related to the subject of which Professor Garner had spoken.

He would like to mention a few types, first the phenolic type, derived from phenol and formaldehyde, which was by far the most important of all. The phenols were derived from coal, either direct or from benzene, and, while the benzene might be produced in the United States from hydroforming in the petroleum industry, in this country there was no doubt that it would always be produced from the coal-gas industry. The formaldehyde would probably be produced by the dehydrogenation of methanol or, in the petroleum industry, by the catalytic oxidation of methane. Apart from the fact that these were the first resins to be produced on a really large scale, their pre-eminence was due to their cheapness, their ease of moulding, and their structural strength. One of their disadvantages was that they were rather dark in colour, but that had been improved within the last year or eighteen months. The products from the phenolic type of plastic included moulding powders, laminated products with paper or fibre base, castings for further working and solutions in drying oils for the paint and varnish industry.

There were also the alkyd type, the amino type, and the acrylic and the polystyrene types of plastics, all derived, partly at least, from the petroleum industry, and he was quite sure that, as time went on, more and more plastics would be built up from the starting gases of the petroleum industry.

Aromatic petroleum extracts were again mixtures in the petroleum industry formed when lubricating oils were extracted; they were used partly as drying oils and partly as fillers. Naphthenic acids were other materials which were made on a large scale, as were also sulphonates, but he had not time to refer to those substances at any length.

In conclusion, he would like to direct attention to the different meaning which the chemistry of petroleum had for the present audience as compared with members of the Institution of Petroleum Technologists fifteen or twenty years ago. In those days, the early days of cracking, those engaged on the refinery side used to have a very useful little item at the end of their balance sheets, known as "gas and loss." Who in those days ever dreamed that that item would really be the beginning of an enormous chemical industry? The gases were now almost the sole source of *iso*-octane, and very soon, he suggested, aeroplanes would be running on nothing but what was made out of those gases.

An enormous vista was opened out to the petroleum industry. Looking back on the last ten years, would anyone present like to suggest that the research on the chemistry of petroleum or petroleum products was approaching its zenith, let alone its end? Whether the production of various products from petroleum or the various uses to

which those products could be put was considered, the road which was being opened up was, to his mind, only at its beginning, and no indication could be given as to which way the road would branch. Petroleum, the raw material for this chemical industry, was only beginning to be understood. In the past far too much of it had been burned, and it was high time that research workers considered more and more closely how this precious raw material could best be conserved so that not one cubic foot of it was lost to the service of mankind. There was too great a tendency at present to squander raw-material resources. He had recently seen in a paper the suggestion that the roofs of houses in the future should be made of stainless steel. Why should such precious materials be used except in places where there was no alternative? He hoped that those engaged in the petroleum industry would get rid of any nonsense of that sort in their industry. They should ensure that the greatest and the best possible use was made of the precious raw material which had been entrusted to their care.

In conclusion, he would like to urge the members not to feel that their industry and the coal industry were rivals, but rather that between them they could continue to use for the benefit of mankind two valuable fuels and very precious raw materials, neither of which was inexhaustible.

Mr. Harold Moore said he thought all the members present should be very grateful to the openers of the discussion for having brought such an interesting subject before them, but there was one point which had not been mentioned, *i.e.*, that the whole of the synthetic petroleum industry was entirely dependent on refinery by-products, and unless refining was carried out in this country, he did not know how the raw material could be obtained. With a home consumption of petroleum of 12,000,000 tons a year, there should be about 500,000 tons of C_3 and C_4 hydrocarbons available and 500,000 tons of other gas, which would be sufficient to build a very large industry, as well as providing a certain amount for aviation purposes. He thought that the new development should result in a reconsideration of the attitude which had been adopted so far, which was, he thought, unfavourable to refining in this country and in favour of refining at the fields. The new development ought to alter the whole outlook on the subject.

The field for research opened out to physicists and chemists by the new development was a most entrancing one, and he was sorry to find, from watching the papers carefully for some time, that British physicists and chemists had had much less to do with recent developments than had been the case twenty years ago. It appeared that most of the work on the subject was being done in other countries at the present time.

He had been associated with one particular experiment recently. This experiment had now reached the pilot-plant stage, and was being carried on in equipment somewhat similar to a commercial unit. The plant was engaged in aromatization, a reaction which had been known for a considerable time. In this case the charge was naphtha and other liquid fractions, not gases. A very complete aromatization had been obtained, the liquid product containing approximately 98 per cent. of aromatic hydrocarbons. This process opened up a new field, in that, whereas benzole and toluol were quite easily extracted from coal-tar products, and could be purified simply, some of the higher bodies existing in coal tar were very difficult to isolate and purify. By the process to which he referred, an approximate yield of 10 per cent. of benzole, 10 per cent. of toluene, and 10 per cent. of a mixture of ethyl benzene and xylenes were obtained, and could be purified with little other treatment than simple distillation. Higher aromatic compounds, such as naphthalene, anthracene, acenaphthene, and phenanthrene, were easily isolated from the higher fractions, as there were practically no olefines, oxygen, sulphur, or nitrogen derivatives present in the finished mixture. Sulphur left the reaction as H_2S. Whereas coal tar could be made to yield the simple hydrocarbons at economical costs, it was very expensive to isolate the higher compounds from coal tar, and refined naphthalenes, anthracene, and higher hydrocarbons are very expensive, in spite of being present in considerable quantity in the relatively cheap coal tar. By the aromatization of petroleum these higher bodies could be obtained with much less difficulty. In addition to the liquid aromatic products, C_3 and C_4 fractions were given in the gaseous state, and were largely unsaturated. The pitch yield was about 4 per cent. He did not consider the process as a substitute for coal tar, but it was particularly advantageous for making higher hydrocarbons, and made available an extra supply in case the demand for benzole and toluol exceeded the quantity

available from coal tar. The amount of phenol extracted from coal tar might prove insufficient in view of the development of the plastic industry. Even when phenol was made from coal-tar benzene, the yield might still be insufficient. The method he described provided another way of obtaining increased production over and above the coal-tar production.

DR. BRANCKER said he did not agree with Mr. Moore that most of the research on petroleum was being done outside this country. He thought that a considerable amount of it was being done in this country, but, owing to the necessity for secrecy, the results of the research were not available. He himself had been engaged on research and, although he could mention what he had been doing, he was prevented from giving full details about it. In time of war he thought there should be a pooling of knowledge, and if that took place Mr. Moore would be shown to be incorrect in his opinion as to the amount of research that was going on in this country.

The question that he wished to discuss was that of aromatic petroleum residues. Dr. Dunstan had said that the coal-tar industry would be superseded by the products obtained from petroleum, and he did not think anyone present would disagree with that. Dr. Dunstan had outlined the manner in which he was building up very interesting bodies, but, besides being built up, they could also be obtained by the process of breaking down, and he wished to direct attention to the fact that aromatic petroleum residues contained a considerable percentage of aromatics, naphthenes, and paraffins. A considerable amount of work had been done in Manchester on the constitution of aromatic petroleum residues, with the use of what was known as the Vlugter, Waterman Van Westen method of analysis. That method of analysis had certain limitations, and there might be criticisms of it, but he thought it gave a very fair approximation of the chemical constitution of the aromatic petroleum residues. Those residues were being used extensively for rubber and for drying oils, but they were used at present in the dark, in a "hit-and-miss" way. Sometimes they were successful and sometimes they were unsuccessful. It was desirable to have more knowledge on the subject of what particular aromatic petroleum residues would suit a particular purpose, and with that in view their chemical constitution had been ascertained at Manchester, about thirteen oils altogether having been dealt with. The research workers there had concentrated on three main extracts. The first one showed on analysis that it contained three benzene rings in the form of an anthracene nucleus, to which was attached one *cyclo*pentane ring and a C_8 paraffin, but it was not known just how the rings were combined. The raffinates which corresponded to the extracts contained a low percentage of aromatics and high percentage paraffins. In the first case it contained one benzene nucleus, as compared with the three in the extract, a *cyclo*naphthene C_8 and a paraffin chain C_{17}. It was found that the extracts were not unsaturated in an aliphatic sense, but neither had they what was called a diene number. There were anthracene, benzene, and naphthalene nuclei in the extracts; therefore why had not the extracts a diene number? The answer given was that the paraffins were distributed around the nuclei masking the double bonds, but the research workers at Manchester could not be sure about that; all that they could advance at present was the constitution of the extracts in percentages of aromatics, paraffins, naphthenes. They suspected that the aromatic petroleum residues had a certain structure from molar volumes, but further than that they could not go at present. It was possible that, if the results of the research were published, someone more academically minded might be able to say what particular fraction of an extract could be used for rubber manufacture, etc., from a knowledge of molecular structures.

With regard to the use of aromatic petroleum residues as drying oils, what it was desirable to do now was to make the extracts more unsaturated, introducing if possible the double bonds which were so essential in organic chemistry, and that could be done, for example, by chlorinating the extract and then drying off the hydrochloric acid, in effect dehydrogenation. The oil then had an entirely different physical nature; it was viscous and tenacious before, and if put on a glass plate nothing happened, but if the dehydrogenated extract was put on a glass plate, it formed a kind of film, which he thought indicated a drying product. It was along lines such as these that a drying oil could probably be made.

He thought it would be agreed that a fairly good advance had been made in the subject.

Dr. Underwood said that he would like to emphasize a point which had been brought up by Mr. Moore. It had to be admitted that the bulk of the work described in the discussion that afternoon had been done abroad, particularly in America, although there were, of course, notable exceptions. One such exception with which all the members were familiar was the pioneer work carried out by Dr. Dunstan and his colleagues on the alkylation process. It must not be taken as a sign of the inferiority of British scientists and technicians that this position had arisen. It resulted from the absence in this country of a vigorous refining industry to provide an adequate training-ground for technicians in the processes in question. It might be argued that it would be uneconomic and impracticable to have such a training-ground in this country, because the oil was not found here and the refining should be done where the oil was found, but, if that argument was carried to its logical conclusion, there would not be a cotton industry in this country because cotton was not grown here, there would be only a very small woollen industry because not much of our wool was produced here, and even the iron and steel industry in this country would be a very insignificant one. Without a flourishing industry as a training-ground technicians could not be trained, just as people could not be taught to swim without a swimming-bath. Facilities for practical experience were essential.

The opening contributions to the discussion had to cover such a wide field that it was almost inevitable that there should be omissions. No reference had been made to the development of the nitroparaffins. This was still in its infancy, but might well lead to an industry comparable in magnitude with that based on the nitro-aromatics. Another important process which had not been mentioned was the conversion of methane and other lower hydrocarbons into acetylene. This had been carried out on a modest scale before the war, and was being carried out on a larger scale to-day. It was obviously a very important development, not merely because it produced another substance to add to the list but also because it produced a substance which was the starting-point of a very large number of well-established industries. When the petroleum industry produced a material like acetylene, which was the starting-point of a number of existing and important industries, that development was much more important than if there was produced merely another product which in itself might be useful but which was not the starting-point for many other processes of manufacture. The same argument applied to the aromatization processes for producing the aromatic hydrocarbons in pure form from petroleum, because that meant in effect that anything which was now produced from the coal-tar hydrocarbons could be produced from petroleum hydrocarbons if they were converted to benzene, naphthalene, anthracene or any of the other hydrocarbons which were at present based on coal tar.

Dr. R. C. Fisher said he would like to touch upon one point, which had not been mentioned by any of the previous speakers, in connection with the modern developments under discussion. So far it was essentially the chemical aspect of the subject which had been discussed, but he would like to say a few words on the engineering aspect, because obviously the chemical developments must be assisted by adequate engineering. Engineering, he thought, was both a handicap, to a certain extent, and a great help to the modern developments in question. It might be surprising to hear engineering referred to as a handicap, but, when Dr. Dunstan criticized Nature for producing butane instead of other more useful compounds, one wondered whether it was not the human mind, more particularly that of the engine designer, which was at fault. If the engine designer could produce a mechanism which would burn the products as they were available in Nature, it would not be necessary to correct Nature and make them better fuels. Engineering could also be a help to the modern developments in question. In the laboratory it was a relatively simple matter to isolate pure hydrocarbons by distillation, but it was a very different matter to isolate pure hydrocarbons on an industrial scale, and he suggested that the fact that it had been possible on a large scale to separate those basic compounds was the reason why it was practicable to proceed along the wide road ahead. The problems to which the oil engineer who had been educated in the old style of refinery processes involving simple distillation and possibly simple cracking, had become accustomed were rather basically changed in the modern field. Not only were the temperatures and the pressures encountered considerably different, but the materials themselves were also very different from an engineering point of view. For instance, the viscosity of all the

light modern products was considerably lower than the viscosity to which one was accustomed in connection with "old style" petroleum products. The net result was that the pumping problems and the lubricating problems were much more difficult. The economic side also required most careful study. For instance, in a refinery where one has available large amounts of waste, the gases, the combustion problems, and combustion engineering were not very difficult; on the contrary, the more one burned of those gases the better; whereas now the chemists laid their hands on most of the constituents of the gases and it was difficult to find anything that one was allowed to burn in a furnace: in other words, higher efficiency was of great importance.

He wished to point out that, unless very great care and research were devoted to the mechanical engineering side, it would be rather difficult for the fuel, chemical, and scientific development to make practical use of the theoretical investigations that could be carried out in the laboratory on a small scale.

THE PRESIDENT suggested that a paper might be read before the Institute on the subject brought forward by Dr. Fisher, and also that another meeting might be held for the further discussion of the question of petroleum as a source of synthetic materials.

DR. DUNSTAN agreed, saying that another meeting might well be held for an open debate on the subject which had been introduced on the present occasion by the openers of the discussion. It was obviously impossible to deal with it adequately at one meeting.

A vote of thanks was accorded to the openers of the discussion, and the meeting then terminated.

THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute was held at the Royal Society of Arts, John Adam Street, London, W.C.2, on Tuesday, 8th June, 1943, at 5.30 p.m. Mr. C. Dalley, the President, occupied the Chair.

PETROLEUM AS A SOURCE OF SYNTHETIC MATERIALS.

The discussion on the subject of "Petroleum as a Source of Synthetic Materials," which had been opened by Dr. Dunstan, Professor Garner, and Mr. Oriel, at the meeting of the Institute held on 25th March, 1943, was resumed.

DISCUSSION.

MR. ASHLEY CARTER said he would be interested to know what were the uses of petroleum for thermo-plastics and for thermo-setting plastics.

MR. W. W. GOULSTON said that, in the making of plastics from petroleum, the unsaturated hydrocarbons which were present in petroleum would be used. Those unsaturated hydrocarbons would polymerize, either in the presence of a catalyst or by just being allowed to stand, into various resin-like compounds. Another method was to react some of the unsaturated hydrocarbons with other bodies, and thus make plastics in the same way as synthetic plastics were made in the ordinary chemical industry. Styrene, for example, which was one of the unsaturated hydrocarbons present in some of the petroleum gases but was more often manufactured by reacting ethylene with benzene and dehydrogenating, polymerized to a plastic. It also combined with other substances to form plastic materials, *e.g.*, it was combined with butadiene to give a particular type of plastic material—namely, synthetic rubber. Buna S was made in that way. One merely needed to indicate the presence of the unsaturated hydrocarbons in the petroleum gases, especially the cracked gases. Cracked materials were the starting-points for various chemical synthetic bodies, including, of course, resins.

DR. A. E. DUNSTAN pointed out that styrene had been identified in the products of the pyrolysis of methane, and that the late Professor Wheeler, Mr. W. H. Cadman and he had drawn attention to this occurrence many years ago.

MR. HAROLD MOORE said that experiments were being carried out at Manchester on the aromatization of petroleum naphthas, and a mixture of xylene, styrene, and benzene was obtained. The benzene and styrene were obtained by dehydrogenating ethyl benzene. The proportions were very difficult to ascertain, and there was some difficulty in the conversion to styrene of ethyl benzene. Quite reasonable yields were obtained; the total production, he thought, was about 9 to 10 per cent. of the naphtha, and about two-thirds of it was either ethyl benzene or styrene. In the catalytic treatment the temperature used was below 700° C.

THE CHAIRMAN said that in the last number but one of the *Journal* he had seen a statement by Dr. Gustav Egloff that all synthetic materials discovered in organic chemistry could be made from methane and that there were half a million of them.

MR. HAROLD MOORE said he had happened to get the catalogue of Carbide Chemicals of the United States recently, and it was surprising to see the large number of synthetic products made from petroleum. The list gave one some idea of what was happening in the United States at the present time with regard to the manufacture of synthetic products from petroleum, especially petroleum gases. There were about fifteen alcohols in the list, up to heptadecanol—methyl, ethyl, *iso*propyl, and so forth. There were six glycols, and there were ethers and oxides, there being a range of about eight glycol ethers, and there were also butyl ethers, and so on. There was a range

of about eight esters, which included some of the glycol esters, and there were also about ten ketones, six aldehydes, and four organic acids. The firm had not listed such things as formic acid and acetic acid. There were four anhydrides, eight chloride compounds, such as butyl chloride, a range of about thirty amino-compounds, including quite complex ones, a series of sulphates and a range of pure hydrocarbons. The whole list comprised about 120 products, all in commercial production and made in large quantities. The Company had another list of chemicals made in research quantities.

He thought the main plastics made from petroleum were those made from ethylene, isobutylene, butadiene, and styrene, the two most important of those being styrene and butadiene.

Carbide Chemicals were specializing particularly on the vinyl resins, and they sent out a notice with their catalogue saying that one could put sticky fingers on it and wipe it with a wet cloth and it would be perfectly all right, because it had vinyl polymer on the outside.

Mr. J. S. Jackson thought the hope of the future was that either formaldehyde or aceylene would be produced from methane. Methane was a substance that was available in enormous quantities, whereas the other basic materials under consideration usually involved manufacturing processes such as cracking. He had seen references in the literature to the practical possibility of producing formaldehyde from methane by oxidation and acetylene by heat treatment.

Mr. W. W. Goulston said that the question of manufacturing acetylene or formaldehyde from methane was an economic and commercial one, the cost of that method of manufacture having to be compared with the cost of other methods. He had no doubt that very large sums of money were being spent in supporting research work, particularly in the United States, for finding an economic commercial method of manufacturing acetylene and formaldehyde from methane. As Mr. Jackson had pointed out, methane was available in enormous quantities, and acetylene and formaldehyde were extremely useful materials as starting-points for a very large range of synthetic products.

Mr. Harold Moore said that the Cities Service Company had a large plant manufacturing formaldehyde from methane, but he did not know of any large-scale manufacture of acetylene from methane, the latter being a more difficult process.

Mr. J. S. Jackson said he believed that at present the Americans depended to a considerable extent upon natural gas for their domestic heating, but it seemed to him that in a very short time everything that would burn would be regarded as a basic material for the manufacture of synthetic resins or chemicals and people would then have to freeze, but they would have nice chairs to sit on and pretty rooms to freeze in.

Dr. A. E. Dunstan said that the amount of petroleum produced in the whole world was about the same in weight as the amount of coal produced in Great Britain —*i.e.*, about 250,000,000 tons a year. The methane problem was exceedingly intriguing. There might be, he thought, about 10,000,000 tons of methane produced in a year. He had been assured many years ago by Lord Cadman that, apart from petroleum methane, there was a colossal amount of methane wasted in the gases pumped out of coal mines in the ordinary ventilation from mines, and the opinion had been expressed that there was probably more methane associated with coal than there was with petroleum.

Methane was a most recalcitrant hydrocarbon. It was so symmetrical that one did not know where to attack it, but he was inclined to think that methane to acetylene was the best line of attack, acetylene being a convenient source of many valuable products.

There was another aspect of synthetic petroleum chemistry which might be of interest to the members—namely, the synthetic chemistry of food. It was a well-known fact that in the last war Germany produced a certain amount of fatty acids by the oxidation of waxes, and it was also well known that, as Professor

Williams had shown, the production of glycerol from propylene was straightforward enough. Having obtained glycerol and stearic acid, one found the way to food substances fairly open, and he had heard it suggested that it was not beyond the bounds of possibility for organic chemists to synthesize materials of the vitamin type. With glycerine, stearic acid, and a certain modicum of synthetic vitamins, one would have a first-class foodstuff.

Mr. Harold Moore said that the present production of gas was over 70 million tons a year, but that, of course, was not all methane, as it included ethane, propane, butane, etc. He believed it had been recently said that the United States production of gas was about 30 per cent. of the production of oil (he presumed that applied generally to the rest of the world), and that the reserves of gas were something approaching 100 per cent. of the reserves of oil in tons. The largest consumption for plastic at the moment was for rubber, which should take about 1 million tons.

Mr. H. L. West, referring to Dr. Dunstan's remarks about making glycerol from propylene, said he thought they gave rise to the question whether it was not desirable to use the petroleum gases available for synthesis in the best possible way. Glycerol could be made quite easily by fermentation, and he thought it would be better to make it in that way and to use propylene for other purposes.

Another point that struck him was that in order to produce the unsaturated gases it was usually necessary to employ a relatively large proportion of raw petroleum as a heating medium; the process was a somewhat wasteful one in its consumption of petroleum as a raw material. He thought one of the main lines of investigation now should be to find a method of producing the unsaturated gases without such a waste. He looked forward to an advance being made in biochemical processes whereby it would be possible to produce some of the gases required, probably saturated, in sufficient quantities to augment the production from petroleum, utilizing materials not so exhaustible as petroleum.

He thought it was time that the gas industry started to use some of the knowledge that was available from the petroleum industry in order to conserve some of the materials that were at present burned in coal gas. He believed there was a small proportion of ethylene burned in coal gas which, if removed, might make a very useful starting material for synthetic rubber.

He believed it had been stated recently that the rate of consumption of petroleum at the moment was so high that some of the fields in the United States were beginning to become exhausted.

Mr. W. W. Goulston said that the suggestions made by Mr. West were quite sound. A number of products could be made by fermentation, and he had no doubt that many new processes would be worked out in the future which at present were not even dreamed of, but up to the present most of the starting materials for fermentation processes were foods and substances which could be used for food. In the United States very large quantities of grain were being used for manufacturing butadiene, and the farmers there were very anxious for it to be used for that purpose, but he thought it was quite wrong. At present, of course, the situation was very difficult, and food could not always be taken to the places where it was wanted, so there was probably an excess of food in certain parts of the world, but when the times were more normal food should be used for food, and not as a starting material for synthetic products.

With regard to Mr. West's point that it was wasteful to produce unsaturated hydrocarbons from petroleum, because a great deal of petroleum was required to make a very small quantity of unsaturated hydrocarbons, he thought Mr. West had probably lost sight of the fact that the process also resulted in the production of commercial petroleum products.

Mr. Harold Moore said he did not agree that it was wasteful to make glycerol from propylene. The cost of propylene was about £2 a ton, whereas none of the fermentation products was in that range at all. Most of the propane used to-day was used as a substitute for fuel. As far as the thermal efficiency of the change-over from propane to propylene was concerned, the reactions were not very wasteful ones. The fermentation industry used a colossal amount of fuel in the preparation of ethyl

alcohol in order to get it distilled to the concentration required, and he believed the amount of heat recovered was very small in proportion to the amount used in the distillation process. Glycerol was about £100 a ton, most of the synthetic materials being £50 to £100 a ton. The gases, even when extracted, were only £2 a ton, and when sold in bulk the price was much lower; yet it was suggested that they should be burned and not used for making glycerol.

Dr. A. E. Dunstan said that Williams had authoritatively stated that the price of glycerol made synthetically compared very favourably indeed with the price of glycerol made by fermentation. To obtain glycerol by the ordinary fat-splitting methods involved the utilization of foodstuffs, whereas the synthetic manufacture made use of what was in effect largely a surplus product.

He would like to point out to Mr. Goulston that the unsaturated hydrocarbons used in synthetic chemistry were almost invariably products of petroleum which were incidental to the main purpose of making motor spirit.

Professor F. H. Garner said that, with reference to the general question of natural products competing with petroleum products, one very important point which would have to be considered was what would happen to all the rubber plantations in Malaya and other places when rubber was made from petroleum or alcohol. There was a large population concerned in the rubber industry, and their future means of livelihood would have to be taken into consideration. He believed that question was being studied at the moment by a Colonial Products Committee.

With regard to the question of the most economical source for the various synthetic materials, that would be settled in due course. It resolved itself into a question of the cost of labour and the various processes which were involved. The point as to whether alcohol should be derived from agricultural products or from petroleum would have to be settled on a world-wide basis in the long run.

It should be remembered that when petroleum was cracked the whole of the products were utilized. It was not cracked specifically for the production of butadiene, for instance. The process was modified so that butadiene could be produced in large quantities, but the other products produced at the same time were, of course, utilized for fuel and other purposes.

The President said that the oil companies in Trinidad had to pay a subsidy to assist the sugar industry in that country, so if it was necessary to rely for alcohol made from sugar produced in Trinidad there would have to be financial assistance from some source other than oil companies.

Mr. H. L. West thought his remarks had been somewhat misunderstood. His point was that the petroleum supply was definitely exhaustible. It appeared that in about two hundred years' time, with the increasing consumption of petroleum for different purposes, mainly as a fuel, there would be a definite shortage. Therefore he thought that, as a long-range policy, the oil companies should institute research to see whether the raw materials for making synthetic products could be derived from other sources, such as vegetable material.

Dr. A. E. Dunstan suggested that when that unhappy time came when petroleum was becoming scarce there would be illimitable amounts of shales. The Americans had made a very accurate survey of the shale resources in the United States, and they were gigantic. When the shales were exhausted he imagined that the coal industry would step into the breach.

Mr. Harold Moore suggested that if the supplies of petroleum were likely to become exhausted it would be better not to use it in ships and motor cars, but to reserve it for synthesis, where any given quantity went so much further. A million tons of petroleum was a very large amount from the point of view of making synthetic materials. If a man was short of petrol and butter he would probably prefer to have a gallon of butter than a gallon of petrol, because a gallon of petrol would not go very far, but eight or nine pounds of butter would.

The President said that just before the war maize was being burned under boilers in Venezuela. There was a possibility of employing vegetable materials or edible

materials when it was economic to do so and to utilize petroleum when it was economic to do so. Edible materials might even be cultivated for the specific purpose.

He was sorry that Mr. Dewhurst was not present, because he could have dispelled the bogey that was so often raised about the end of petroleum being in sight. It had been shown, for instance, that the Athabasca tar-sands of Canada would last for a very long time. He did not think there was any need to be alarmed about the supplies of petroleum coming to an end, and there were vast areas in many places which could grow corn, maize, and so on, which could be utilized if and when it was economic to do so. The Russians were using grain for the purpose of making butadiene on a large scale, but they were very anxious to produce large quantities of foodstuffs also.

Mr. Ashley Carter said he would like to ask Professor Garner a question on the subject of rubber production from the tree. He had been fortunate enough to see rubber trees planted in the early years of the present century, and he thought it took about three years from the time of planting for a rubber tree to reach the tapping stage—*i.e.*, the stage when the latex could be tapped from the tree. After three years the girth of a rubber tree was about 9 inches. How would the cost of the rubber produced from them compare with the cost of synthetic rubber?

Professor F. H. Garner said he could not answer Mr. Ashley Carter's question about the girth of the rubber trees, but, with regard to the question of cost, he thought it was estimated that the cost of producing natural rubber was about the same as that of producing synthetic rubber.

The important point to bear in mind, in his opinion, was that some of the new synthetic rubbers would be very superior to natural rubber in a number of respects. Some of them, as was well known, were far superior from the point of view of oil resistance, and others were said to be superior from the point of view of wear when used for tyres. That made the competition with natural rubber more severe than it would be if the synthetic product was identical with natural rubber.

Mr. Harold Moore said that the price of butane was £2 to £5 a ton and the price of rubber was about £100 a ton, and between those two limits a technical and very new process had to be carried out. He thought that if engineers and chemists were left long enough with a proposition of that kind they would finally be able to work with a very much narrower margin than at the present time. The controlling factor was how great the margin was between raw butane and butadiene rubber. In other synthetic processes the cost of production had decreased very rapidly after the first period of testing out production, and it looked as if the petroleum product would be a very severe competitor with the natural product in so far as it fulfilled the requirements.

Dr. A. E. Dunstan said that the synthetic production of indigo was a case which illustrated very clearly Mr. Moore's remarks.

ESTIMATION OF MERCAPTAN SULPHUR ALONE OR IN PRESENCE OF ELEMENTARY SULPHUR IN PETROLEUM PRODUCTS.*

By E. R. H. Davies, Ph.D., A.I.C. (Member), and
J. W. Armstrong, B.Sc.

Introduction.

The publishing of this method is sponsored by Sub-Committee No. 3 of the Institute of Petroleum, having in mind the possible inclusion in later editions of the Handbook.

No originality is claimed for the method—in fact, it is understood that in a modified form it is in use in the Emeryville (and probably other) laboratories of the Shell Development Co. and in Universal Oil Products, Ltd.

It was felt that publication in the *Journal* would lead to possible constructive criticism out of which could be evolved a method considerably more satisfactory than the present qualitative "Doctor" test. The method has been in constant use in the laboratories of the authors and has given every satisfaction.

Available Methods.

(*a*) *Iodometric Method* [1, 2].—This method depends on the oxidation of mercaptan to disulphides by iodine solution :

$$2\,RSH + I_2 = RSSR + 2HI$$

This method, however, fails in the presence of olefins and oxidizing and reducing agents interfere.

(*b*) *Lamp Method before and after Sweetening.*—This method has been used in conjunction with various sweetening processes,[3, 4, 5] but is rather time-consuming, and not too reliable in presence of organic sulphides and disulphides.

(*c*) *Mercuric Chloride Method* [2].—This method is based on the reaction :

$$RSH + HgCl_2 \longrightarrow RSHgCl + HCl$$

the HCl being titrated. It has been shown, however, that mercuric chloride reacts with olefins to liberate acid.[6]

(*d*) *Cupric Chloride Method* [7].—Here the mercaptans are quantitatively oxidized to disulphides with cupric chloride. $2\,RSH + CuCl_2 \longrightarrow RSSR + Cu_2Cl_2 + 2HCl$. The cuprous chloride is titrated with potassium permanganate. The chief limitation to this method is that it must be carried out in the absence of air. It is also not applicable to coloured solutions.

* This method has been submitted to and discussed by Standardization Sub-Committee No. 3—Liquefied Petroleum Gases, Gasoline, Kerosine, and Light Distillates. It was felt that the method was of considerable general interest, and its publication was therefore suggested.

(*e*) *Cupric Oleate Method.*[8]

$$4\ RSH + 2\ Cu(OL)_2 \longrightarrow 2\ CuSR + RSSR + 4H(Ol)$$

This method is not suitable in the presence of peroxides nor in coloured solutions.

(*f*) *Silver Nitrate Method*[4].—The precipitation of silver mercaptide would seem to be the most favoured method. This method is still rather tedious, as the tendency of the silver mercaptide to pass into the hydrocarbon phase and carry with it adsorbed silver nitrate necessitates lengthy washing. The principal objection, however, is that excess silver nitrate is used, and in consequence all anions whose silver salts are insoluble are precipitated, along with the mercaptans. It is also unsuitable for coloured solutions. Some improvement may be obtained by adding methanol,[9] which decreases the tendency of the solutions to form emulsions.

(*g*) *Potentiometric Methods*[10].—Tamele and Ryland found that using alcohol to dissolve the sample and titrating with an alcoholic solution of silver nitrate, the separation of phases, the formation of emulsions, and the resulting adsorption are completely eliminated. Furthermore, to avoid excess silver nitrate at the end of the precipitation, the end-point is determined potentiometrically with a silver electrode, thus making the method applicable to coloured solutions. Also on account of the very low solubility of silver mercaptide, the method is applicable in the presence of substances, which normally react with silver nitrate, but form compounds more soluble than the silver mercaptide.

Principle of Proposed Method.

The method is an adaptation of that proposed by Tamele and Ryland.[10] It depends on: (*a*) the extreme insolubility of silver mercaptides and silver sulphide in alkaline solution and the relatively greater insolubility of silver sulphide compared to silver mercaptides; (*b*) the interaction of elementary sulphur, mole for mole, with mercaptan sulphur producing silver sulphide through an intermediate sodium alkyl disulphide as shown by the equations below. The end-points of titration are determined by measuring the change in potential of a silver electrode immersed in the titration vessel by a potentiometric procedure.

For mercaptans alone, the mechanism can be represented by:

$$RSH + Ag^+ \rightleftharpoons AgSR \downarrow + H^+$$

Sodium acetate is used as an alkaline buffer to prevent loss of mercaptan and to neutralize the hydrogen ion formed during titration of the mercaptans. For mercaptans plus elementary sulphur the suggested mechanism is the formation of mixed sodium alkyl disulphide which reacts with the silver ion to yield finally silver sulphide and alkyl trisulphide thus:

$$S + RSNa \rightleftharpoons NaSSR$$
$$2\ Na\ SSR + 2\ Ag^+ \rightleftharpoons Ag_2S \downarrow + R_2S_3 + 2Na^+$$

Scope.

The method is applicable to the determination of mercaptan sulphur and elementary sulphur in colourless, or coloured petroleum products. It is

not affected by olefins, aldehydes, peroxides, inert sulphur compounds, dyes, phenols, naphthenic acids, fatty acids, nitrogen bases, or chloride ion. Hydrogen sulphide must be removed before making the determination.

Apparatus.

A simple arrangement for the potentiometric titrations is shown in Fig. 1. The cell consists of a silver half-cell, which is sensitive to changes in silver ion concentration and a mercury half-cell which serves as the reference electrode. The silver half-cell consists of a silver wire, 2 mm. in diameter, with its lower half immersed in a beaker containing 50 mls.

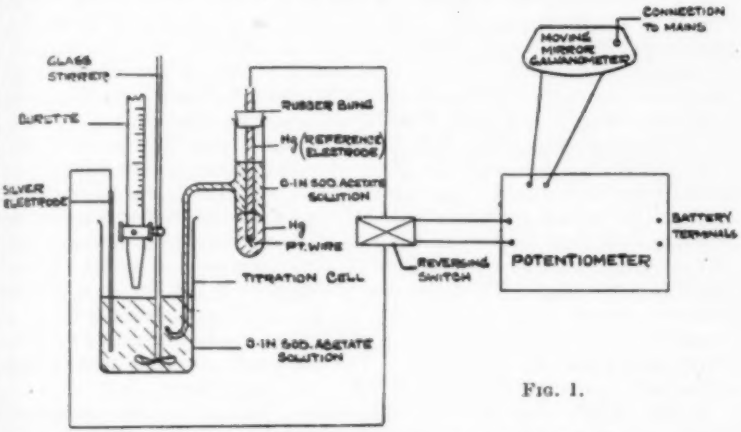


Fig. 1.

of 0·1*N*-sodium acetate in 95 per cent. ethyl alcohol. The mercury half-cell consists of a glass tube closed at one end and bearing a side-arm midway along its length, bent as shown in sketch to form the bridge. The end of this side-arm is drawn out to a very fine orifice, terminating beneath the surface of the solution in the titration cell. The mercury half-cell contains a layer of mercury approximately 1½ inches deep, with the standard 0·1*N*-sodium acetate solution above it. The level of the sodium acetate solution is adjusted so that it is about ½ inch above the side-arm when the bridge is full of the solution and the rubber bung tightly in position in the top of the cell (see Fig. 1). The reference electrode consists of a suitable piece of soda glass tube closed at one end with a small length of platinum wire sealed in, the tube being filled with mercury. The electrical lead makes contact by dipping into the top surface of the mercury.

A reasonably sensitive potentiometer arrangement is required that will measure potential differences of one millivolt.

A suitable assembly is made by connecting a moving mirror galvanometer in series with a "Unipivot" Potentiometer supplied by Cambridge Instrument Co., Ltd.

The apparatus also includes a glass stirrer, 10 ml. burette calibrated in 0·05-ml. divisions, and a reversing switch.

Reagents.

0·1*N*-sodium acetate solution in 95 per cent. ethyl alcohol.

0·01*N*-silver nitrate solution in ethyl alcohol, containing 10 per cent. water. This solution is prepared from a stock solution of 0·1*N* strength by diluting 10 mls. of 0·1*N*-silver nitrate solution (aq.) to 100 mls. using absolute alcohol.

Acid cadmium sulphate solution, containing about 15 gm. cadmium sulphate and 1 ml. 12*N*-sulphuric acid per 100 mls. of solution.

Procedure.

If hydrogen sulphide is present, a sufficient volume of oil sample is first shaken with cadmium sulphate solution until a small portion of the treated sample no longer gives any yellow colour or precipitate with fresh reagent. An appropriate volume of treated oil sample is then added to 50 mls. of the alcoholic sodium acetate solution in the silver half-cell, so as to provide a titration range of 5–10 mls. of 0·01*N*-silver nitrate solution.

The initial reading of the E.M.F. between the electrodes is recorded, and then suitable integral amounts of the standard silver nitrate solution are added from the burette. *After each addition sufficient time must be allowed to elapse for the cell to establish an unchanging potential before recording the readings.* In the region where the E.M.F. changes slowly as increments of silver nitrate solution are added, 0·5-ml. portions may be added between the E.M.F. readings. When the rate of change of E.M.F. becomes greater, however, the potential-volume readings should be made every 0·1 ml. A graph is made by plotting E.M.F. readings as ordinates and ml. of standard silver nitrate solution as abscissae. The end-points are taken in the middle of the steep portions of each break in the potential volume curve.

In the slightly alkaline, buffered solution of sodium acetate, mercaptans react mole for mole with elementary sulphur to form sodium alkyl disulphide. If no elementary sulphur is present the initial E.M.F. of the cell (before any silver nitrate is added) is approximately—400 millivolts and a curve like that labelled (*a*) in Fig. 2 is obtained.

$$\text{In this case, RSH as S \% by wt.} = \frac{(\text{mls. } AgNO_3 \times \text{normality} \times 32{\cdot}06)^*}{\text{gm. oil sample} \times 10}$$

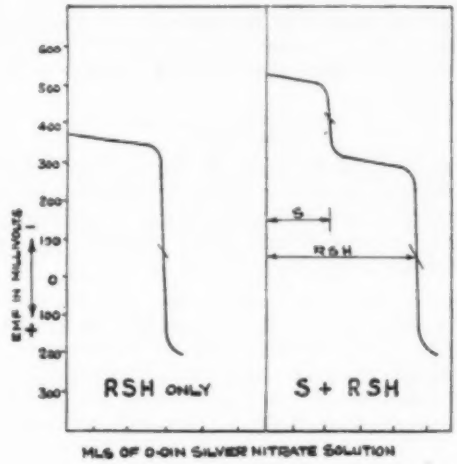
If elementary sulphur is present along with the mercaptans, however, the initial E.M.F. will be approximately —600 millivolts. When mercaptan sulphur is in excess of the elementary sulphur, two end-points will be found, as in curve (*b*), Fig. 2. The first represents the end of the precipitation of alkyl disulphide ion, since the corresponding silver compound is less soluble than silver mercaptide.

$$\text{In this case, elementary S (\% by wt.)} = \frac{(\text{mls. } AgNO_3 \text{ to first break})\,(N)\,(32{\cdot}06)}{\text{gm. oil sample} \times 10}.$$

$$\text{RSH as S (\% by wt.)} = \frac{(\text{total mls. } AgNO_3 \text{ to second break})\,(N)\,(32{\cdot}06)}{\text{gm. oil sample} \times 10}.$$

* One equivalent of silver nitrate is equal to one equivalent of sulphur.

When the elementary sulphur is in excess, only one end-point will be obtained, in which case a measured amount of a standard solution of *n*-propyl mercaptan must be added to the sample before titration. The procedure and conditions are then the same as in the previous case. Sufficient mercaptans must be added to give a distinct mercaptan break in the volume-potential curve.



(*a*) FIG. 2. (*b*)

In this case, elementary S (% by wt.) =

$$\frac{(\text{mls. } AgNO_3 \text{ to first break})\ (N)\ (32{\cdot}06)}{\text{gm. of oil sample} \times 10}.$$

RSH as S (% by wt.) =

$$\frac{(\text{total mls. to second break} - \text{mls. for added RSH})\ (N)\ (32{\cdot}06)}{\text{gm. of oil sample} \times 10}.$$

NOTES.

The importance of keeping the silver electrode perfectly clean cannot be too strongly stressed. The electrode should be cleaned with potassium cyanide and washed carefully with distilled water.

Although rapid equilibrium is generally attained during the titration, the equilibrium becomes slow at the stage of the titration where a "break" occurs in the potential-volume curve. During this stage of the titration it is generally necessary to wait several minutes before adding the next increment of silver nitrate solution. Erroneous values will result if an additional increment is added before an unchanging potential is obtained.

The precipitation is made in alcohol solution because this eliminates the tendency of the silver mercaptide to occlude silver nitrate—as it does in water solution—and leads to high results.

The apparatus described here, although simple, has been found to be very effective, and the results are reproducible.

The method may be extended to the determination of mercaptans in liquefied petroleum gases, by externally cooling the titration beaker to −15° C. by the use of "drikold"; the sample, depending on its mercaptan content, being quickly weighed into the chilled beaker on a trip scale or by means of a previously chilled pipette.

The method is also capable of further extension to include the estimation of hydrogen sulphide alone or in the presence of elementary sulphur or mercaptan sulphur. This, however, is considered an unnecessary complication, due to the ease with which a sample can be freed of hydrogen sulphide.

Precision.

The relative accuracy depends on (*a*) the solubility of the sample in alcohol, and (*b*) the amount of silver nitrate consumed by the sample. The end-point of the titration can be determined with an accuracy of ± 0·02 c.c. This indicates 2×10^{-7} mole of mercaptan. Therefore if 10 c.c. of sample are taken, the precision should be :

Molality.	% RSH in sample.	% error.
0·1	1·0	±0·02
0·01	0·1	±0·2
0·001	0·01	±2·0

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Imperial Chemical Industries, Ltd.,
Billingham.

THE FILTER FREEZING TEMPERATURE OF AVIATION FUELS.*

By J. M. A. Court, B.Sc., A.I.C.

Definition.

When a fuel flows under controlled conditions through a wire gauze filter of defined dimensions, the highest temperature at which the rate of flow falls below a specified critical value is defined as the filter freezing temperature.

General Considerations.

Certain proposed blends of aviation fuel having a high water solubility, tend to precipitate ice at low temperatures, with resultant freezing or blocking of the filter screens of aircraft fuel filters. This method provides a means of determining the tendency of such fuel to cause filter freezing.

The type of gauze and the conditions of flow chosen for this test are based on a study of the standard 200-g.p.h. filter, which is one type of filter now used in aircraft. This filter has for its filter screen two concentric cylinders of wire gauze, the inner member being made of 80 × 80-mesh gauze, and the outer member of 100 × 120-mesh gauze. The total effective gauze area is approximately 17·2 square inches, and for simplification, and to impose slightly more severe conditions on the laboratory test, it has been assumed that the whole of this area is composed of 100 × 120-mesh gauze. The rate of flow, although not a very critical factor, is based on these figures, and for the filter used in this method amounts to approximately 50 mls. per minute.

Apparatus.

Fuel Container.—Shall be a suitable bottle having a capacity of approximately 1300 mls. and dimensions close to those shown in the diagram (Fig. 1). It should be closed by a tightly fitting rubber bung having three holes for the thermometer, the air-vent and the outlet tube. It shall be supported so that the fuel level is 2 feet 6 inches above the delivery jet when flow commences.

Cooling Bath.—Shall be a suitable Dewar flask of 6 inches inside diameter and 11 inches deep, into which the fuel container can be placed for cooling.

Air Drying Tube.—Any suitable tube containing calcium chloride may be used, provided that the latter is not so tightly packed as to cause any back pressure on the fuel flow.

Wire Gauze Filter.—Shall consist of a brass tube of dimensions indicated in the diagram (Fig. 1), with wire gauze securely soldered over one end. The gauze shall be soldered on the outside only of the brass tube, and there shall be no blockage of the effective area of the gauze by solder. The thimble thus formed shall be a sliding fit on glass tube of dimensions 10 mm. outer diameter and 7 mm. inner diameter, and shall be secured in

* This method has been submitted to and discussed by Standardization Sub-Committee No. 3—Liquefied Petroleum Gases, Gasoline, Kerosine, and Light Distillates. It was felt that the method was of considerable general interest, and its publication was therefore suggested by the Sub-Committee.

APPARATUS FOR DETERMINING THE FILTER FREEZING TEMPERATURE OF AVIATION FUELS.

FIG. 1.

position with the end of the glass tube in contact with the gauze by means of a petrol-resisting rubber or a suitable jointing compound. The filter shall be constructed with brass gauze of the following dimensions :—

100 × 120 mesh. 100 mesh to be of 41-s.w.g. wire (0·0044 inch dia.).
120 mesh to be of 40-s.w.g. wire (0·0048 inch dia.).

Thermometer.—Shall be an alcohol thermometer reading in units of 1° C. from +30° C. to −80° C. The alcohol column shall be visible to −50° C., with the bulb at least 3 inches below the fuel level in the container when the latter is full.

Capillary Tube.—The delivery jet offers little restriction to fuel flow, and control of the latter shall be obtained by inserting a capillary tube in the circuit. This capillary tube shall be of such a bore and length that with a head of 2 feet 6 inches of fuel on the delivery jet, the flow through the latter shall be 50 mls. per minute at laboratory temperature.

Procedure.

About 1500 mls. of the fuel to be tested shall be saturated with water by shaking with the latter in a Winchester quart bottle for 15 minutes at laboratory temperature. The sample shall be allowed to stand 24 hours until it is free from suspended water, and it shall then be transferred to the fuel container by syphoning through a 100 × 120-mesh wire-gauze filter to ensure that no solid material enters.

The fuel shall be cooled gradually over a period of 2 hours to the desired temperature in the cooling bath with alcohol and solid carbon dioxide. When the fuel has been maintained at this temperature for 15 minutes, the flow shall be started by applying suction to the delivery jet, after which it shall be allowed to proceed by syphoning. The rate of flow shall be checked and recorded at 5-minute intervals by measuring the volume in mls. collected per minute in a measuring cylinder.

The rate of flow will decrease slightly, due to the drop in gravity head of fuel, but the onset of filter freezing is indicated by a marked and sudden decrease in flow, which may eventually cease completely. The fuel fails if at any time during the test the flow falls below 25 mls. per minute.

Tests shall be carried out first at 0° C. and thereafter in decrements of 10° C. down to −50° C., using a freshly water-saturated sample of fuel for each test. The highest temperature at which the flow falls below the critical value of 25 mls. per minute shall be reported as the filter freezing temperature. Immediately after each test the filter shall be removed from the fuel container and examined for the presence of ice.

Precautions.

The highest points of the glass tubes leading from the fuel container to the delivery jet are liable to trap air bubbles which may be hidden by the coating of ice which is formed on the outer walls when testing at low temperatures. These air-locks, if allowed to persist, will cause a large decrease in flow which will confuse the results. Care must therefore be taken to remove the trapped air and to prevent further locking.

The author wishes to express his thanks to the Ministry of Aircraft Production for kind permission to publish this method.